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ON SOME ADDITION-REACTIONS OF THIO ACIDS.

BY HENRY L. WHEELER.

Received June 3, 1901.

The appearance of an article by A. Eibner[1] on a halogen-substituted aminomercaptan, in which some addition-reactions of thioacetic acid to compounds containing the unsaturated grouping C=N are described, has induced the writer to publish an account of some experiments which have been done here along similar lines. In the article referred to, it is shown that thioacetic acid acts on trichlorethylidendiphenamine,

$$CCl_3CH(NHC_6H_5)_2,$$

with the formation of acetanilide, hydrogen sulphide and a compound which is said to have the properties of acetylphenyl-α-aminotrichlorethyl mercaptan. It is also stated that benzylidenaniline unites with thioacetic acid to form the addition-product, $C_6H_5CH(SH)NC_6H_5.COCH_3$.

It was shown by Wheeler and Barnes[2] that the phenylhydrazone of diethylthiocarbonic ester, $C_6H_5NH—N=C(SC_2H_5)OC_2H_5$, reacts with thiobenzoic acid, yielding ethylthiolbenzoate, $C_6H_5CO.SC_2H_5$, and phenylthiolcarbazinic ethyl ester,

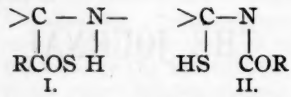
$$C_6H_5NH—NHCO.SC_2H_5.$$

This reaction evidently involves a sort of addition different from

[1] *Ber. d. chem. Ges.*, **34**, 656 (1901).

[2] *Am. Chem. J.*, **24**, 62 (1900).

that described by Eibner. These two modes of addition can be represented as follows:



I. II.

The ease with which Eibner's addition-products give acetanilide indicates that the addition takes place according to (II). The possibility, however, that they may have the structure $RCH(SCOCH_3)NHC_6H_5$, and that the addition takes place according to (I) is not excluded by the evidence thus far produced.

Chanlaroff[1] found that thioacetic acid combines with the $-C\equiv N$ group in thiocyanates; and in papers from this laboratory it has been proved that the addition takes place according to (II),

$$CH_3COSH + RSCN = CH_3CONHSCSR.$$

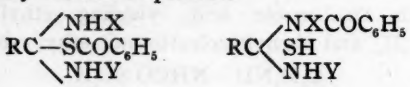
It has been shown by Wheeler and Merriam[2] that isothiocyanates, RN=CS, in general, react readily and quantitatively with thioacetic and thiobenzoic acid, even in boiling benzene, yielding substituted amides and carbon disulphide.

The final result of the action in this case is in all probability preceded by the formation of an unstable addition-product, according to (II), which decomposes as follows:

$$C_6H_5N{=}CS + HS.COC_6H_5 = C_6H_5CO(C_6H_5N\boxed{CSS}H.$$

This is confirmed by the fact that thiobenzoic acid and phenyl isocyanate give the addition-product, $C_6H_5CO(C_6H_5)NCOSH$, which can easily be isolated. It may be crystallized from alcohol, and is stable at temperatures below 97°.

Thiobenzoic acid unites with amidines, and, as might be expected, quite stable addition-products or salts result. Whether the addition takes place according to the first method, giving esters of thiolbenzoic acid (III), or according to the second, with the formation of diamidomercaptan derivatives (IV), can not be definitely decided at present.



III. IV.

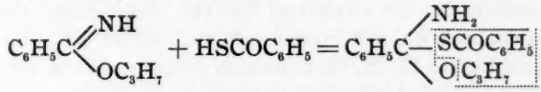
[1] *Ber. d. chem. Ges.*, **15**, 1987 (1882).

[2] This Journal, **23**, 283.

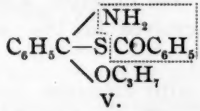
The evidence thus far obtained appears to favor the view that the addition takes place as represented by (III). Such a compound would not separate hydrogen sulphide without decomposition, while if the products have the structure (IV), or are simple pentavalent nitrogen derivatives, they might easily be desulphurized.

The addition-product in the case of diphenylformamidine decomposes on fusion, with evolution of little more than traces of hydrogen sulphide, into thioformanilide and benzanilide. Alkalies remove thiobenzoic acid and not hydrogen sulphide.

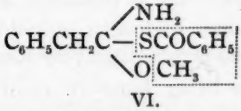
The above view receives further support from the behavior of imidoesters. Thiobenzoic acid readily reacts with imidoesters, and the products are a thiol ester and an amide. The reaction evidently takes place by addition to the double union according to I, as in the case of the above-mentioned phenylhydrazone. It may be represented as follows:



That the decomposition proceeds in the above manner, and not as represented by (V), is shown by the behavior of phenylacetimidomethyl ester towards thiobenzoic acid (VI):



V.



VI.

The amide obtained in the latter case is phenyl acetamide, instead of benzamide, and consequently the esters formed in these reactions are thiol and not thion derivatives.

An analogous reaction takes place in the case of acylpseudothioureas. Benzoylpseudobenzylphenylthiourea gave benzoylphenylthiourea, when heated on the water-bath with thiobenzoic acid:

$$C_6H_5CON{=}C(SCH_2C_6H_5)NHC_6H_5 \rightarrow C_6H_5CONHCSNHC_6H_5.$$

Thiobenzoic acid readily reacts with acetonephenyl hydrazone, on the steam-bath in an entirely different manner from that of benzoyl chloride[1], and the mixture shows very little loss in weight. *s*-Monobenzoylphenylhydrazine separates in quantity, while only a small amount of dibenzoylphenylhydrazine is

[1] Freer: *Am. Chem. J.*, **21**, 18 (1899).

obtained. In addition to this, considerable neutral oil results which cannot be purified by distillation under diminished pressure. The thio acid acts in this case, therefore, according to (II).

The action of thiobenzoic acid on ureas has been examined in the case of diphenylthiourea. It has been shown by Deninger[1] that, in the presence of pyridine, benzoyl chloride and this urea give a dibenzoyl derivative, while, according to Dains,[2] to produce a reaction without pyridine it is necessary to heat the materials to a high temperature. At 150° phenyl mustard oil and benzanilide are quantitatively obtained.

I have found that thiobenzoic acid acts on this urea in boiling benzene, and that the action is similar to that of benzoyl chloride, although the products obtained are benzanilide, carbon disulphide, hydrogen sulphide, and regenerated diphenylthiourea.

The action can be explained by the assumption that the thiourea contains a C=N group, and that either addition takes place according to II, or, that the acid decomposes the urea into aniline and phenyl mustard oil as the first stage of the reaction.

It has been found, in regard to the use of thiobenzoic acid as a means of introducing the benzoyl group into aryl amines, that it reacts as easily as thioacetic acid[3]. For example, when mixed with aniline, hydrogen sulphide is evolved in the cold, and benzanilide is quantitatively formed.

On the other hand it combines with ammonia and alphyl amines to form more or less stable salts. The product of the union of thiobenzoic acid and diisobutyl amine, $C_6H_5COSH.HN(C_4H_9)_2$, can be repeatedly crystallized from alcohol without evolution of hydrogen sulphide. A similar behavior of the phenylsulphocarbazinic acid salts of aryl and alphyl amines, $C_6H_5NH—NHCS.SH.H_2NR$, has been observed by Busch and Rider.[4] The former give thiosemicarbazides while the alphyl salts do not. Thiobenzoic acid also reacts on the steam-bath with alcohols and phenols, forming benzoic esters.

EXPERIMENTAL PART.

Benzoylthiolcarbanilic Acid, $C_6H_5CO(C_6H_5)NCO.SH$.—When a

[1] *Ber. d. chem. Ges.*, **28**, 1322 (1895).
[2] This Journal, **22**, 192 (1900).
[3] Pawlewsky: *Ber. d. chem. Ges.*, **31**, 661 (1898).
[4] *Ber. d. chem. Ges.*, **30**, 843 (1897).

benzene solution of phenyl isocyanate (3 grams) and thiobenzoic acid (3.5 grams) were mixed, heat was evolved and the yellow color of the thio acid disappeared. On cooling, a mass of fine colorless needles separated. These, crystallized from alcohol, melted at 97°–99° with effervescence and a nitrogen determination gave:

	Calculated for $C_{14}H_{11}O_2NS$.	Found.
Nitrogen	5.44	5.35

When this compound was heated, it gave off a combustible gas (COS) and on crystallizing the residue from alcohol, benzanilide melting at 161° was obtained.

Alcoholic ammonia converts this addition-product into ammonium thiolbenzoate and phenylurea.

When thioacetic acid was added to para-tolyl isocyanate under similar conditions para-acettoluide was directly obtained.

Diphenylformamidine and Thiobenzoic Acid (by Bayard Barnes).—When 3 grams of the amidine were dissolved in benzene and 2.1 grams of thiobenzoic acid were added, a mass of colorless needles separated, weighing 4 grams. These melted at 130°–131° and could be crystallized from benzene or a mixture of benzene and ligroin, with only slight decomposition. A nitrogen determination gave:

	Calculated for $C_{20}H_{18}ON_2S$.	Found.
Nitrogen	8.38	8.56

Two grams of this addition-product were melted in an oil-bath at 145°–150°. On cooling and treating the mass with dilute sodium hydroxide a residue remained which crystallized from alcohol in plates melting at 160°–161° (benzanilide). On adding hydrochloric acid to the alkaline extract a precipitate was obtained which crystallized from alcohol in plates and melted at 137°–138° (thioformanilide). When the addition-product was treated with alkali, diphenylformamidine was obtained.

Benzenylmonophenylamidine and Thiobenzoic Acid (by Bayard Barnes).—This product crystallized from benzene in yellowish-white needles and melted at 141°–142°. A nitrogen determination gave:

	Calculated for $C_{20}H_{18}ON_2S$.	Found.
Nitrogen	8.38	8.50

Benzenylphenylparatolylamidine and Thiobenzoic Acid (by

Bayard Barnes).—The amidine was prepared from benzanilide-imide chloride and paratoluidine. On mixing this in benzene with thiobenzoic acid a pale yellow precipitate separated, melting at 131°–132°. A nitrogen determination gave:

	Calculated for $C_{27}H_{24}ON_2S$.	Found.
Nitrogen	6.60	6.68

This compound did not decompose as smoothly, on heating, as that in the case of diphenylformamidine. The yellow product soluble in alkali as well as that which was insoluble was a mixture. In all probability both thiobenzanilide and thiobenztoluide were formed.

Benzimidonormalpropylester and Thiobenzoic Acid (by William Valentine).—Thirty grams of the imido ester were treated with 25.5 grams of thiobenzoic acid at 0°. A solid separated and on allowing the mixture to warm a little the solid melted and a reaction took place with the formation of a precipitate. This weighed 18.5 grams and it crystallized from alcohol in tables which melted at 128°. A nitrogen determination gave 11.5 per cent. of nitrogen, while the calculated for *benzamide* is 11.5 per cent.

The oil removed from the above weighed 36 grams. It was taken up in ether, shaken with dilute alkali, washed, dried, and distilled at 16 mm. pressure. The portion boiling at 130°–150° was distilled at ordinary pressure whereupon the larger portion boiled at 251°–255°, a little distilling above 255°. A sulphur determination in the former agreed with the calculated for *n-propylthiolbenzoate*, $C_6H_5CO.SC_3H_7$.

	Calculated for $C_{10}H_{12}OS$.	Found.
Sulphur	17.8	17.6

Phenylacetimidomethyl ester and Thiobenzoic Acid (by William Valentine).—Twenty-five grams of the ester and 24 grams of thiobenzoic acid reacted immediately. The solid material that separated weighed 15 grams, it was crystallized from alcohol whereupon it melted at 154°–155° and a nitrogen determination agreed with the calculated for *phenylacetamide*, $C_6H_5CH_2CONH_2$:

	Calculated for C_8H_9ON.	Found.
Nitrogen	10.37	10.37

The oil from the above contained benzyl cyanide and was not obtained in a pure condition.

Acetonephenylhydrazone and Thiobenzoic Acid (by William Valentine).—Thirty grams of the hydrazone and 28 grams of thiobenzoic acid were warmed for a number of hours on the steam-bath, whereupon some solid material (22 grams) separated and the loss in weight was about 1 gram. The solid material crystallized from alcohol in small prisms and melted at 168°–169° and a nitrogen determination agreed with the calculated for *benzoylphenylhydrazine*.

	Calculated for $C_{13}H_{12}ON_2$.	Found.
Nitrogen	13.1	13.0

On adding ether to the oil filtered from the above about 2 grams of solid material separated which, on crystallizing from alcohol, melted at 176°–177° and contained no sulphur. A nitrogen determination agreed with the calculated for *dibenzoylphenylhydrazine*.

	Calculated for $C_{20}H_{16}O_2N_2$.	Found.
Nitrogen	8.8	8.8

The ether solution of the oil was shaken with soda and then with dilute hydrochloric acid, whereupon about 10 grams of unaltered hydrazone were obtained. The remaining oil decomposed on attempting to purify it by distilling at reduced pressure.

Methyl Alcohol and Thiobenzoic Acid.—Ten grams of thiobenzoic acid and 25 cc. of methyl alcohol were boiled for twenty hours. The alcoholic solution was then treated with water and a little sodium bicarbonate, whereupon 7 grams of methylbenzoate boiling at 198°–200° were obtained. Calculated yield, 9.9 grams. The action of thiobenzoic acid and phenol under the same conditions was much slower.

Diisobutylammoniumthiolbenzoate, $C_6H_5COSH.HN(C_4H_9)_2$. — When the calculated quantity of thiobenzoic acid was added to diisobutyl amine, cooled in a freezing-mixture, the material solidified to a crystalline mass, while only a very little hydrogen sulphide was evolved. On crystallizing the material twice from alcohol it formed beautiful colorless flattened prisms which melted in a closed tube at 124°. A nitrogen determination gave:

	Calculated for $C_{15}H_{25}ONS$.	Found.
Nitrogen	5.24	5.43

This salt dissolved in water, and silver nitrate gave a pure white precipitate which blackened on boiling.

NEW HAVEN, CONN., May 31, 1901.

STUDIES ON SOLUTIONS OF STANNOUS SALTS, III.

By S. W. Young.

Received April 4, 1901.

PART I. THE COURSE OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

IN a previous paper[1] it was pointed out that there were two probable courses which the reaction between stannous chloride and free oxygen, in presence of hydrochloric acid, might take; *viz.*,

$$SnCl_2 + 2HCl + O = SnCl_4 + H_2O \qquad (1)$$

and

$$SnCl_2 + 3H_2O + O = Sn(OH)_4 + 2HCl. \qquad (2)$$

It was also suggested that it might be possible to determine which of the two reactions was the one actually occurring, since if stannic chloride were first formed it would afterward slowly hydrolyze and thereby, on account of the formation of free hydrochloric acid in the solution, one would observe a gradual increase in the conductivity of the solution for some time after the oxidation was complete. Among others Kohlrausch[2] has recently investigated the change of conductivity with the time, in freshly prepared solutions of stannic chloride, and found that for dilute solutions, the increase was quite noticeable, but lasted for only a comparatively short time, when the conductivity became practically constant. In stronger solutions (about half-normal) the increase in the conductivity was still perceptible after several days.

The following investigations were carried out in the hope of applying this phenomenon to the determination of the presence or absence of stannic chloride in freshly oxidized solutions of stannous chloride. In order that the results might be as conclusive as possible several oxidizing agents besides oxygen were investigated. Among these a somewhat special interest is attached to sodium hypochlorite, since Thomsen[3] found that with this oxidizing agent he obtained a very constant value for the heat of oxidation of stannous chloride, whereas with chlorine the values obtained were very irregular. One might surmise from this that the course of the oxidation was somewhat different in the two cases.

[1] This Journal, 23.

[2] Ztschr. phys. Chem., 33, 257.

[3] "Thermochemische Untersuchungen," II, 445.

The results of the research are classified as to the oxidizing agent used. The general method was to oxidize the solution as rapidly as possible, transfer it to a conductivity flask and begin measurements as soon as the solution had acquired the temperature of the thermostat. The solution for oxidation was freshly prepared for each experiment. The hydrochloric acid concentration was varied in different experiments for reasons which will appear. The concentration of the stannous chloride was the same in all experiments, *viz.*, 2 grams of the crystallized salt in 100 cc., *i. e.*, about 0.16 normal. (Titrations gave results as follows: 0.1625, 0.1623, 0.1630.)

All measurements were made in a thermostat at 25° C. The results cannot be used as a measure of isothermal reaction velocity, because, on account of lack of proper facilities, it was necessary to allow the thermostat to cool down each night.

1. OXIDATION BY MEANS OF FREE OXYGEN.

Solutions 0.1, 0.2, 0.3, 0.4, and 0.5 normal in hydrochloric acid were investigated. Since the oxidation ordinarily goes very slowly, all oxidations with free oxygen were accelerated by means of small quantities of hydrogen sulphide.[1] The time required for oxidation was from five to fifteen minutes, according to the acid contents of the solution.

Following are the tabulated results of the measurements with free oxygen. T is time in hours and K is specified conductivity in reciprocal ohms.

A. MEASUREMENTS WITH 0.1 NORMAL HCl.

1.[2] T =	0	1/6	2	4	19	21		
K =	0.05999	0.06071	0.06159	0.06210	0.06247	0.06285		
2. T =	0	1/12	1/6	1/2	1	3	5½	24½
K =	0.0797	0.0813	0.0818	0.0824	0.0837	0.0845	0.0853	0.0869
T =	62	105	125					
K =	0.0880	0.0880	0.0880					

B. MEASUREMENTS WITH 0.2 NORMAL HCl.

1. T =	0	1⅙	4½	6	23½	25½
K =	0.1140	0.1165	0.1180	0.1192	0.1192	0.1195
2. T =	0	14½	19½	24	68½	92
K =	0.1123	0.1168	0.1212	0.1220	0.1223	0.1223

[1] This Journal, **23**, 144.

[2] In this experiment only 1 gram of stannous chloride per 100 cc. was used. In all others 2 grams were used.

C. MEASUREMENTS WITH 0.3 NORMAL HCl.

1. T =	0	1/6	22½	28	47½	97½	120	142
K =	0.1010	0.1297	0.1523	0.1530	0.1540	0.1544	0.1544	0.1544

D. MEASUREMENTS WITH 0.4 NORMAL HCl.

1. T =	0	1/12	1/6	¼	⅓	½	3
K =	0.1313	0.1390	0.1405	0.1423	0.1433	0.1464	0.1625
T =	4	4½	18½	21	72	120	
K =	0.1661	0.1670	0.1783	0.1802	0.1818	0.1838	

E. MEASUREMENTS WITH 0.5 NORMAL HCl.

1. T =	0	1/6	½	23	28½	48
K =	0.1454	0.1460	0.1850	0.1910	0.1967	0.2064
T =	72½	97½	120	143		
K =	0.2110	0.2132	0.2160	0.2175		

From a consideration of the above results, it is apparent that in all cases there is an increase in the conductivity of these solutions with the time. Further, this increase is greater for solutions more concentrated in hydrochloric than for those less concentrated. This increase is very rapid at first, but its rate rapidly lessens. Thus it will be seen that a difference of a few minutes in the manipulation at the start makes a very considerable difference with the value of the total increase observed, but will have but little influence upon the total time required for the conductivity to become constant. Thus the greater length of time required for attaining equilibrium is more characteristic for concentrated solutions than is the absolute value of the increase in conductivity. In most cases the latter value is also greater for concentrated than for dilute solutions. The phenomena on the whole correspond almost exactly to those observed by Kohlrausch[1] upon dilution of stannic chloride with water, and there can be little doubt but that the oxidation of stannous chloride by free oxygen leads primarily to the formation of stannic chloride which then hydrolyzes, more rapidly in dilute than in concentrated solution. Thus the surmise made in a previous paper[2] that the oxidation leads directly to the formation of stannic or metastannic acid is not confirmed.[3]

2. OXIDATION BY MEANS OF POTASSIUM BICHROMATE.

The method of operation in this case (as in all following ones) was to weigh out the stannous chloride, add a requisite amount of

[1] *Loc. cit.*
[2] *Loc. cit.*, p. 133.
[3] c. f. Thomsen: *loc. cit.*

hydrochloric acid, oxidize with the dissolved oxidizing agent (in this case potassium bichromate), and finally to bring the solution to required volume with water. It was then placed in the conductivity flasks, and measurements made as before. The specific conductivities in this case are naturally considerably less than when the solutions were oxidized with oxygen, on account of the conversion of hydrochloric acid to potassium and chromium chlorides.

F. MEASUREMENTS WITH 0.2 NORMAL HCl.

1. T =	0	1/12	1/6	1/3	1/2	1	1½	16½	20½	24
K =	0.0645	0.0650	0.0665	0.0665	0.0668	0.0674	0.0676	0.0698	0.0700	0.0702

G. MEASUREMENTS WITH 0.3 NORMAL HCl.

1. T =	0	1/12	1/6	1/2	1	2	21	55	
K =	0.0898	0.0923	0.0928	0.0943	0.0958	0.0960	0.1000	0.1011	
T =	98	122							
K =	0.1011	0.1011							

H. MEASUREMENTS WITH 0.5 NORMAL HCl.

1. T =	0	1/12	¼	½	1½	20½	24½
K =	0.1192	0.1222	0.1263	0.1303	0.1357	0.1547	0.1552
T =	54	97	122				
K =	0.1585	0.1585	0.1585				

3. OXIDATION BY MEANS OF FERRIC CHLORIDE.

Only one set of measurements was made with ferric chloride as oxidizing agent, and that with 0.1 normal hydrochloric acid as follows:

I. MEASUREMENTS WITH 0.1 NORMAL HCl.

1. T =	0	1/12	1/6	¼	2½	4¾
K =	0.1053	0.1123	0.1153	0.1178	0.1327	0.1377
T =	24	28	61	104		
K =	0.01515	0.1522	0.1570	0.1581		

It will be noticed that the increase here is very much more marked than in other experiments with 0.1 normal hydrochloric acid. The explanation lies very near, since the reaction between stannous chloride and ferric chloride is in itself a slow one.[1] The method of procedure was somewhat varied in this case in that the amount of a given ferric chloride solution necessary to oxidize the stannous solution was determined from preliminary experiments and this amount added to the solution under investiga-

[1] Noyes: *Ztschr. phys. Chem.*, **16**, 546.

tion. The measurements show, however, an increase in the conductivity long after the reduction must have become complete, and the results for ferric chloride lead to the same conclusions as for other substances.

4. OXIDATION BY MEANS OF HYDROGEN PEROXIDE.

Three series of measurements were made with hydrogen peroxide, upon solutions respectively 0.1, 0.3, and 0.5 normal in hydrochloric acid. A somewhat special interest attaches to these experiments, since if the course of the oxidation with hydrogen peroxide showed itself to be different from that with free oxygen, we should have direct evidence that the oxidation by means of free oxygen was not brought about by the intermediate formation of hydrogen peroxide. As the results show, however, the course of the oxidation is the same with hydrogen peroxide as with free oxygen. Naturally this fact can in no way be taken as evidence that in the oxidation by free oxygen, hydrogen peroxide is an intermediate product. Following are the results of these measurements:

J. MEASUREMENTS WITH 0.1 NORMAL HCl.

T =	0	1/12	¼	1	23	29½
K =	0.0827	0.0837	0.0852	0.0881	0.0930	0.0932
T =	44	48	72½	144	168	192
K =	0.0940	0.0943	0.0950	0.0958	0.0963	0.0963

K. MEASUREMENTS WITH 0.3 NORMAL HCl.

T =	0	1/12	¼	7/12	1	3	6½	20½
K =	0.1223	0.1270	0.1311	0.1368	0.1395	0.1435	0.1527	0.1550
T =	25	49½	122	146	170	194	218	
K =	0.1574	0.1583	0.1613	0.1616	0.1618	0.1622	0.1622	

L. MEASUREMENTS WITH 0.5 NORMAL HCl.

T =	0	¼	¾	2½	5¾	20	24
K =	0.1477	0.1503	0.1523	0.1595	0.1705	0.1883	0.1927
T =	49	122	146	170	194	218	290
K =	0.2045	0.2157	0.2190	0.2213	0.2224	0.2238	0.2253

5. OXIDATION BY MEANS OF SODIUM HYPOCHLORITE.

Two series of measurements were made with sodium hypochlorite, in solutions containing respectively 0.1 and 0.3 normal hydrochloric acid. The sodium hypochlorite was prepared by passing chlorine through cold dilute sodium hydroxide. As was mentioned at the beginning of this paper, some special interest

attaches to these measurements, since the heat of oxidation of stannous chloride by means of hypochlorite was found by Thomsen to give very definite results, while those with chlorine were quite variable. The results given below show, however, that hypochlorite forms no exception to the other reagents studied, in regard to the course of the reaction. Into a probable explanation of Thomsen's results upon the basis of these results, we will not at present enter.

M. MEASUREMENTS WITH 0.1 NORMAL HCl.

T =	0	1/12	1/6	5/12	1	1½	29	53	149
K =	0.1152	0.1180	0.1192	0.1216	0.1233	0.1243	0.1320	0.1326	0.1329

N. MEASUREMENTS WITH 0.3 NORMAL HCl.

T =	0	1/12	¼	½	1	29
K =	0.1319	0.1338	0.1357	0.1386	0.1410	0.1710
T =	53	149	173	197	121	
K =	0.1766	0.1830	0.1838	0.1850		

SUMMARY OF RESULTS.

In all cases examined the freshly oxidized solutions of stannous chloride show electrical conductivities which increase with the time. This increase is in general greater for solutions more concentrated in hydrochloric acid than for those less concentrated. These phenomena are, to all appearances, identical with those noted by Kohlrausch,[1] and are, it seems to me, to be considered as giving indisputable evidence as to the course of the reaction between stannous chloride and the various oxidizing agents used. The conclusion to be drawn from these phenomena is that the first stage in the oxidation of stannous chloride is the formation of stannic chloride, and that for this purpose hydrochloric acid is necessary. In a previous paper[2] this question was taken up speculatively and certain evidence given which led to the surmise that the reaction took place in a somewhat different manner. As a result of the experimental evidence here given this surmise is shown to be wholly unfounded. The two equations given in the ordinary chemical nomenclature, expressing the two reactions in question, are as follows:

$$SnCl_2 + O + 3H_2O = Sn(OH)_4 + 2HCl \qquad (1)$$

and

$$SnCl_2 + O + 2HCl = SnCl_4 + H_2O. \qquad (2)$$

[1] *Loc. cit.*
[2] *Loc. cit*

Reaction (2) is followed by :

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl. \qquad (2a)$$

The evidence shows distinctly that the reaction takes place according to (2) and (2*a*), which latter reaction is the cause of the increasing conductivity of the oxidized solutions with time.

The settling of this question adds one more case to those of reactions which follow the Ostwald rule[1] that "wherever an intermediate product can be formed during a reaction such product is formed," or in other words, the general tendency is for reactions to take place stepwise where possible.

The conclusion reached as a result of the preceding determinations is thus of fundamental importance in the correct formulation of the reaction-velocity in the case of the oxidation of stannous chloride with free oxygen. Part II of this paper will be devoted to a brief preliminary discussion of this point.

PART II. THE KINETICS OF THE REACTION BETWEEN STANNOUS CHLORIDE AND OXYGEN.

1. In a previous paper[2] the velocity coefficients for the reaction between stannous chloride and free oxygen in the presence of varying quantities of hydrochloric acid, were calculated upon the assumption that the hydrochloric acid did not enter directly into the reaction; *i. e.*, that its action was either catalytic, or else due to its influence upon the degree of hydrolysis of the stannous chloride. The values of the coefficients so calculated increased with the time in all cases. Since from the nature of the reaction the concentration of the hydrochloric acid must be greater at the end than at the beginning of the reaction, hydrolytic and catalytic influences could well explain the phenomenon. The catalytic explanation has the advantage over the hydrolytic one in that the phenomenon occurs in concentrations of hydrochloric acid so great that the hydrolysis of the stannous salt cannot well be considered to be very large. However, the results given in the first part of this paper show clearly that neither explanation is sufficient since the hydrochloric acid enters into the reaction as a definite reagent according to the laws of mass action, although it is, of course, by no means excluded that both catalytic and hydrolytic influences may also be at work.

2. Leaving hydrolytic and catalytic influences out of consider-

[1] *Zischr. phys. Chem.*, **22**, 307.
[2] This Journal, **23**, 119.

ation for the present, and considering that the oxygen concentration is constant, we obtain as an expression for the reaction velocity the equation

$$\frac{dx}{dT} = K(A-x)^m(B-x+\Phi[x])^n, \qquad (1)$$

where A is the initial concentration of stannous chloride, and B that of hydrochloric acid, and Φ is a function to be discussed later. For the exponents m and n we should set as most probable values, $m = 1$, $n = 2$, although it is not unlikely that $n = 1$.

3. The form of the function Φ is not determinable from any data at hand. Its value depends upon the rate of hydrolysis of stannic chloride in varying concentrations of hydrochloric acid. Kohlrausch[1] found that, in all probability, this reaction takes place according to a somewhat complicated law. For a somewhat simplified case, however, an expression for Φ is deducible. This case occurs when the primary reaction (the oxidation) is relatively slow, and the secondary one (the hydrolysis) very rapid. A low concentration of hydrochloric acid favors both conditions. In such an ideal limiting case $\Phi = 2$, since for each equivalent of hydrochloric acid used up, two are formed. Our equation then becomes

$$\frac{dx}{dT} = K(A-x)^m(B+x)^n. \qquad (2)$$

By means of the integrated form of this equation I have calculated the velocity coefficients for the reaction in question, upon the assumption that $m = 1$ and $n =$ either 1 or 2. In no case was a satisfactory set of values obtained, all series showing distinctly increasing or decreasing values of K with the time. The natural explanation is that the condition that $\Phi = 2$ is not sufficiently approximated.

4. Although the above equation (2) does not, for the reason just given, correctly formulate the reaction velocity in the case under consideration, there is, nevertheless, no reason theoretically, why reactions should not occur which would be correctly formulated by it, the sole condition being that the secondary reaction should occur at a rate relatively very large in comparison with the primary one. As a matter of fact the equation has been repeatedly used for the formulation of catalytic reactions in cases where one of the products is a catalysor; *e. g.*, the hydrolysis of

[1] *Loc. cit.*, p. 275.

methyl acetate.[1] In other words, from the standpoint of formulation, a catalytic reaction of the sort mentioned (hydrolysis of esters) and a reaction such as that under consideration are identical. Thus the reaction between stannous chloride, oxygen, and hydrochloric acid lends some experimental basis to the oft-made assumption that in catalytic reactions, the catalytic influence is, in many cases, due to the action of the catalytic agent in accordance with the laws of mass action, but in such a way that it is regenerated so rapidly that we fail to find evidence that it has gone into the reaction at all. Certain it is, at least, that if in the oxidation of stannous chloride, the subsequent hydrolysis of the stannic chloride were excessively rapid, we should naturally explain the whole influence of hydrochloric acid as catalytic.

5. From the foregoing it is seen that the equation (2) may be brought to apply to reactions in which it is not at all necessary to assume the presence of catalytic influences. Equation (2) may in all cases, with proper choice of A and B, show a maximum for $\frac{dx}{dT}$. Thus the statement made by Ostwald[2] to the effect that such maxima can only occur when catalytic influences are at work, is too broad. Such maxima are, from the foregoing, seen to be possible from a theoretical standpoint where catalytic action is excluded, and the results of the measurements given in a previous paper[3] give ample experimental evidence of their existence in case of a reaction where, at present, it does not seem necessary to assume catalytic action.

6. The perfectly general form of equation (1) for several substances, A_1, A_2, A_3, $\cdots$ B_1, B_2, B_3, would be

$$\frac{dx}{dT} = K(A_1 - x)^{m_1}(A_2 - x)^{m_2}(A_3 - x)^{m_3}\cdots$$
$$(B_1 + \Phi_1[x])^{n_1}(B_2 + \Phi_2[x])^{n_2}(B_3 + \Phi_3[x])^{n_3}\cdots,$$

where A_1, A_2, A_3, are substances disappearing and not reappearing and B_1, B_2, B_3, are substances disappearing but reappearing as the result of secondary action in quantities greater than the quantities disappearing. Such an equation may have a considerable number of maxima and minima, as is determinable by simple algebraic considerations. Theoretically then a series of maxima are possible in a reaction running in two or more stages, when a sufficient num-

[1] See Ostwald: "Lehrbuch", II², p. 245.
[2] "Lehrbuch," II², p. 270.
[3] *Loc. cit.*

ber of substances are taking part in such a way that the concentrations of some of them increase, and this without necessarily assuming catalytic influences. This would, of course, be equivalent to a "periodic" reaction in a homogeneous system. I know of no cases where such periodicity has been observed. It is quite possible that the well-known tendency toward simplicity of reaction may not allow such to occur. The theoretical point is mentioned here merely as a suggestion.

NOTE.

In the first paper of this series, measurements of the electrical conductivity of stannous chloride solutions are given and likewise of the influence of certain substances on the same. In the matter of the influences of potassium chloride upon the conductivity,[1] it was shown that the calculation was one of great uncertainty, so that a measure of the ability of potassium chloride to form complex salts in solution with stannous chloride was difficult to obtain. There is one phenomenon mentioned in that paper, however, which is capable of an interpretation, that, unfortunately, did not occur to me at the time of writing, and that is the marked and ever-recurring decrease in the values of $\frac{\Delta K \times 10^4}{C}$ with increase in C. This is just what would be expected if the association of potassium chloride with stannous chloride was very marked. For such cases we have the equation

$$\frac{(C_{KCl})^m \times (C_{SnCl_2})^n}{C_{(KCl)_m \cdot (SnCl_2)_n}} = K.$$

If K is very small the first portions of stannous chloride will combine almost wholly with the potassium chloride in the solution, and a large reduction of the electrical conductivity will occur. This will be the result until a large portion of the potassium chloride has entered into combination, after which subsequent additions of stannous chloride will produce smaller and smaller decreases and ultimately an increase. This is noticed in the previous paper[2] very distinctly in the results for 0.25 normal potassium chloride and 0.5 normal hydrochloric acid, while the same general tendency is noted in all cases. It is, perhaps, unfortunate

[1] This Journal, **23**, 32.
[2] *Loc. cit.*

that measurements with more dilute hydrochloric acid were not made, as in all probability the phenomenon would have been even more marked in such cases.

This is related here as a bit of evidence tending strongly to confirm the conclusion reached in the previous paper that potassium chloride exhibits a more marked tendency to the formation of complex compounds with stannous chloride in solution than does hydrochloric acid.

STANFORD UNIV., March 20, 1901.

THE REACTION BETWEEN CHLORINE AND AMMONIA.[1]

BY WILLIAM A. NOYES AND ALBERT C. LYON.

Received May 17, 1901.

IN Hoffmann's well-known lecture experiment for the demonstration of the composition of ammonia, the introduction of the ammonia into the tube filled with chlorine, is followed by the addition of dilute sulphuric acid. Some years ago, when performing this experiment, it occurred to one of us that the use of the sulphuric acid was unnecessary, as any excess of ammonia would be absorbed by the large amount of water which is allowed to enter the tube later. The sulphuric acid was accordingly omitted, but with the surprising result that the tube was left only one-sixth full of nitrogen instead of one-third full, as it should have been. Recently an opportunity has been found to give the subject a more careful study.

A glass tube, having a capacity of about 95 cc. and closed at each end with a stop-cock, was prepared. This tube, after cleaning and drying, was filled with chlorine which was generated from manganese dioxide and hydrochloric acid, and washed with water. The gas was passed through the tube from below till the portion escaping was completely absorbed by a solution of sodium hydroxide. After removing the chlorine from the tubes outside of the stop-cocks, aqua ammonia was allowed to enter the tube from above, and, after shaking gently, was followed by water till the residual gas was at atmospheric pressure. The amount of the nitrogen was then determined by filling the tube with water from a burette which was connected with its lower end.

It was soon found that when strong ammonia is used in excess

[1] The work described in this paper forms the subject of a thesis by Mr. Lyon for the degree of Bachelor of Science at the Rose Polytechnic Institute.

the volume of the nitrogen is considerably greater than one-sixth of the volume of the chlorine, and may approach one-third of the volume of the chlorine but never reaches that limit. If, however, a solution containing 0.5 per cent of ammonia is used in such amount as to leave the solution faintly acid, the volume of the nitrogen approaches very closely to one-sixth the volume of the chlorine. If a 2 per cent. solution of ammonium chloride is used instead of the ammonia, the chlorine is almost completely absorbed and the volume of the nitrogen may be as low as only 1 or 2 per cent. of the volume of the chlorine. As will be shown below by quantitative results, the normal reaction between chlorine and ammonia is

$$12NH_3 + 6Cl_2 = N_2 + NCl_3 + 9NH_4Cl.$$

This normal reaction is obtained, however, only when the ammonia is used very nearly in the proportion indicated. If an excess of ammonia is used, it reacts in part with the nitrogen trichloride, giving free nitrogen, in part, probably, giving ammonium hypochlorite.[1]

$$NCl_3 + NH_3 = N_2 + 3NH_4Cl;$$
$$NCl_3 + 2NH_4OH + H_2O = 3NH_4ClO.$$

If, on the other hand, too little ammonia is used, the ammonium chloride formed by the reaction acts, in part, on the chlorine as stated above, with little or no evolution of nitrogen, and the volume of nitrogen liberated will be less than one-sixth the volume of the chlorine.

In studying the reaction quantitatively, the tube described above was covered with dark paper to prevent the action of light on the nitrogen trichloride formed. After filling the tube with chlorine an amount of 0.5 per cent. ammonia solution, equal to from 90 to 95 per cent. of that required by the reaction, was allowed to enter, the tube was shaken gently, and then water of the temperature of the original gas allowed to enter to atmospheric pressure. After gentle shaking a small additional amount of water would enter, indicating that an absorption of some kind had taken place, and the shaking was repeated till no more water would enter. Whether this small final absorption is due to residual chlorine, or to the fact that nitrogen trichloride has an appreciable vapor-pressure and is not quickly absorbed by the water,

[1] Schönbein: *J. prakt. Chem.*, **84**, 386; Fresenius: *Ztschr. anal. Chem.*, **2**, 59.

was not determined. The lower end of the tube was then connected with a burette and the amount of water required to fill the tube gave the volume of the residual nitrogen.

The contents of the tube were then transferred to a separatory funnel containing 10 cc. of benzene,[1] shaken, the benzene separated, and this repeated twice more. The benzene containing the nitrogen trichloride was shaken at once with an excess of a solution of arsenious oxide in sodium bicarbonate, and the excess of arsenious oxide determined with a standard iodine solution. The reaction is

$$3As_2O_3 + 2NCl_3 + 15H_2O = 2NH_4Cl + 4HCl + 6H_3AsO_4.$$

Each atom of chlorine present is, therefore, equivalent to 2 atoms of "available chlorine."[2]

After titration the solution was distilled with an excess of caustic soda and the ammonia in the distillate was determined by means of a standard acid, thus proving that the substance extracted by the benzene was really nitrogen trichloride.

The solution which had been extracted with benzene, and which was, as has been explained, still slightly acid, was titrated with the same ammonia solution first used and the total ammonia required determined:

The results are as follows:

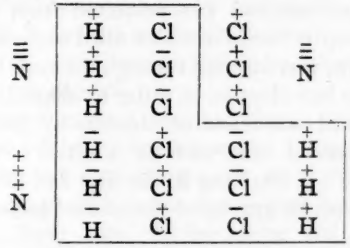
	Calculated.	Found. I.	II.	III.	IV.	V.
Volume of nitrogen as compared with chlorine	16.67	14.32	16.31	17.62	17.20	17.05
Available chlorine.....	50.0	49.3	43.4	35.7	45.5	41.7
Molecules of ammonia per atom of chlorine	1.0	0.97	1.03	1.04	1.01	0.98
Ammonia from NCl_3. Mols. per mol of NCl_3	1.0	0.95	1.10	1.10	1.14	...

Owing to the instability of the nitrogen trichloride and to the secondary reactions which can never be entirely avoided, an exact agreement cannot be expected. The results satisfactorily demonstrate that the reaction already given is the primary one between ammonia and chlorine.

Probably the most interesting feature of the reaction here studied is the fact that 6 molecules of chlorine must react *simultaneously* with 3 molecules of ammonia, for, if the liberation of

[1] Hentschel: *Ber d. chem. Ges.*, 30, 1434.
[2] Hentschel: *Loc. cit.*

nitrogen by the action of 1 part of the chlorine were independent of the formation of nitrogen trichloride by another part, the constant relation of 1 volume of nitrogen to 6 volumes of chlorine would be improbable. The following hypothesis as to the cause of this relationship is given with some hesitation and in the hope that it may lead to discussion and to a further consideration of similar cases. If we suppose, what seems not inherently improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of those molecules, it would follow that elementary molecules, as well, may ionize into positive and negative parts. This explanation of the reaction may be represented graphically thus :



The explanation given involves the further idea that in the ionization of ammonia the hydrogen may become either positive or negative. When we remember the neutral character of ammonia and the fact that its hydrogen may be replaced by either chlorine or sodium, such a thought is not so improbable as it seems when first presented.

That the hypothesis here suggested is capable of a wide application need hardly be said.

TERRE HAUTE, IND., May 15, 1901.

THE BOILING-POINT CURVE FOR MIXTURES OF ETHYL ALCOHOL AND WATER.

BY WILLIAM A. NOYES AND R. R. WARFEL.[1]

Received June 5, 1901.

IT has long been known that it is impossible to obtain absolute alcohol from dilute alcohol by distillation. Some years ago Le Bel[2] showed, also, that a 98 per cent. alcohol could be separated

[1] An account of the work here described was presented to the Faculty of the Rose Polytechnic Institute as a thesis for the Degree of Bachelor of Science.

[2] *Compt. rend.*, 88, 912.

by fractional distillation into an alcohol of 97.4 per cent. (by volume), and a residue containing 99.5 per cent. While these facts demonstrate that the boiling-point of absolute alcohol must be higher than that of alcohol slightly diluted, no one, so far as we can learn, has proved this by means of a direct determination.

The determination of the boiling-point curve for alcohol-water by J. K. Haywood,[1] has come to our notice since reading the proof of this article. Haywood entirely overlooked the minimum point. His curve, from alcohol of 85 per cent. down, agrees satisfactorily with ours.

The boiling-point apparatus of H. C. Jones[2] was used for the determinations. The tube of the condenser was sealed to the side tube of the apparatus, and was protected from the entrance of moisture at the top by means of a tube filled with calcium chloride. A small glass tube was inserted through the cork beside the thermometer, for the introduction of water or alcohol.

The alcohol used was rendered absolute by boiling twice with quicklime, the second time with the addition of a small amount of barium oxide. In distilling it, the first and last portions were rejected. The specific gravity of the alcohol indicated a strength of 99.98 per cent.

The boiling-points for alcohol from 100 per cent. to 64 per cent. were determined with a Beckmann thermometer graduated to $^1/_{100}°$. Those from 64 per cent. to 0 per cent. were determined with a normal Green thermometer graduated in 0.1°. To determine the value of the degrees of the Beckmann thermometer the apparatus was connected with a large flask and a manometer, and the alcohol was boiled under diminished and also under increased pressure. In this way it was found that a difference of 1 mm. in pressure caused, at atmospheric pressure, a change of 0.0333° in the boiling-point. Ramsay[3] and Young's tables give 0.0339° for 1 mm. The value of the degrees was, accordingly, taken as being sufficiently accurate for the present purpose.

To find the value of the Beckmann readings in terms of the true thermometer scale, pure water was placed in the apparatus, and it was connected with a large bottle and a manometer. The pressure was then reduced till the water boiled at about 80° of the true scale and a series of readings of thermometer, barometer,

[1] *J. Phys. Chem.*, **3**, 318.
[2] *Am. Chem. J.*, **19**, 581.
[3] *J. Chem. Soc.* (London), **47**, 640.

and manometer were taken. The barometer and manometer readings were corrected to 0° and by comparison with Regnault's tables for the vapor-pressure of water, the point on the true thermometer corresponding to the readings of the Beckmann thermometer was determined. From this value the boiling-point of absolute alcohol under a pressure of 760 mm. is, as determined by us, 78.33°. The boiling-point calculated from the tables of Ramsay and Young[1] is 78.30°. As Ramsay and Young doubtless had much more accurate means than we could command for measuring heights of manometer and barometer, we have based our tables on their value for the boiling-point, instead of our own.

The barometer used was of the siphon form. The scale was compared with a standard scale by means of a dividing engine before it was filled, and the necessary correction applied. It was filled by ourselves, the mercury being boiled under diminished pressure during the filling.

In carrying out a series of determinations a weighed amount of alcohol or of water, or, in some cases of dilute alcohol, was put into the apparatus and the boiling-point determined. A weighed amount of water or alcohol was then added and the determination repeated. Each time, the barometer and its temperature were also read. The results were then corrected to a basis of 760 mm. by adding or subtracting $^1/_{30}$° for each 1 mm. difference in pressure. The nature of the readings will be apparent from the following illustration. In correcting the barometer readings a plus correction of 1 mm. for error of scale is included.

SERIES 7.

Grams of water added.	Barometer.	Temperature.	Barometer corrected to zero.	Beckman readings.	Beckmann readings corrected to 760 mm.	Per cent. of alcohol.
0.0000	737.6	19.5	736.13	2.948	3.744	99.98
0.2128	737.9	20.0	736.37	2.925	3.713	99.51
0.2440	737.95	20.0	736.42	2.907	3.693	98.97
0.1790	738.0	18.0	736.72	2.895	3.671	98.58
.....	.....	...	.....	....	....	....
.....	.....	...	.....	....	....	....
0.2900	743.5	17.5	742.28	3.089	3.680	92.42
0.2860	743.7	17.5	742.48	3.115	3.699	92.10

Started with 44.478 grams of alcohol of 99.98 per cent.

Six series of experiments, made before the use of the apparatus had been sufficiently mastered, were rejected. Four series

[1] *Loc. cit.*

which gave fairly concordant results were used to obtain mean values for the range from alcohol of 100 per cent. to 92 per cent. From these series the following values for each change of one-half per cent. in the amount of water were calculated by interpolation.

Per cent. of alcohol.	7.	8.	10.	11.	Mean.	
100.0	3.745	3.738	3.756	3.759	3.750	
						0.030
99.5	3.714	3.708	3.727	3.730	3.720	
						0.027
99.0	3.695	3.680	3.700	3.698	3.693	
						0.021
98.5	3.669	3.655	3.687	3.678	3.672	
						0.017
98.0	3.653	3.639	3.674	3.654	3.655	
						0.016
97.5	3.638	3.625	3.658	3.634	3.639	
						0.008
97.0	3.620	3.619	3.651	3.632	3.631	
						0.004
96.5	3.624	3.612	3.643	3.629	3.627	
						0.003
96.0	3.626	3.613	3.633	3.625	3.624	
						0.002
95.5	3.627	3.613	3.634	3.632	3.626	
						0.001
95.0	3.625	3.611	3.638	3.633	3.627	
						0.009
94.5	3.636	3.623	3.647	3.639	3.636	
						0.009
94.0	3.635	3.630	3.660	3.655	3.645	
						0.016
93.5	3.653	3.644	3.678	3.668	3.661	
						0.016
93.0	3.672	3.656	3.698	3.682	3.677	
						0.014
92.5	3.679	3.667	3.713	3.705	3.691	
						0.018
92.0	3.694	3.685	3.728	3.728	3.709	

The remainder of the boiling-point curve possesses less interest and it was not attempted to secure the same degree of accuracy. From alcohol of 92 per cent. to 65 per cent. two series of determinations were made and the Beckmann thermometer was used.

For alcohol from 65 per cent. to 0 per cent., two series were made and the normal Green thermometer was used. As a part of the stem of the thermometer was outside of the apparatus a stem correction from the tables of Rimbach[1] was used. The correction for the thermometer at 100° was determined in the apparatus with pure water and the correction at 80° was determined by comparison with the Beckmann thermometer, whose value had been determined as described above. As the two corrections were different a table of corrections for intervening degrees was calculated on the supposition that the scale of the thermometer was uniform.

The final results of all the series are as follows:

[1] *Ber. d. chem. Ges.*, **22**, 3075.

Per cent. of alcohol.	Boiling-point.	Per cent. of alcohol.	Boiling-point.	Per cent. of alcohol.	Boiling-point.
100.0	78.300	88.0	78.445	55.0	81.77
99.5	78.270	87.0	78.530	48.0	82.43
99.0	78.243	86.0	78.575	37.0	83.76
98.5	78.222	85.0	78.645	35.0	83.87
98.0	78.205	84.0	78.723	29.0	84.86
97.5	78.191	83.0	78.806	26.0	85.41
97.0	78.181	82.0	78.879	22.0	86.11
96.5	78.179	81.0	78.968	20.0	87.32
96.0	78.174	80.0	79.050	18.0	87.92
95.5	78.176	79.0	79.133	13.0	90.02
95.0	78.177	78.0	79.214	10.0	91.80
94.5	78.186	77.0	79.354	8.0	93.10
94.0	78.195	76.0	79.404	7.0	93.73
93.5	78.211	75.0	79.505	5.50	94.84
93.0	78.227	73.0	79.683	4.50	95.63
92.5	78.241	71.0	78.862	3.0	97.11
92.0	78.259	69.0	80.042	2.0	98.05
91.0	78.270	67.0	80.237	1.50	98.55
90.0	78.323	65.0	80.438	1.00	98.95
89.0	78.385	63.0	80.642	0.50	99.65

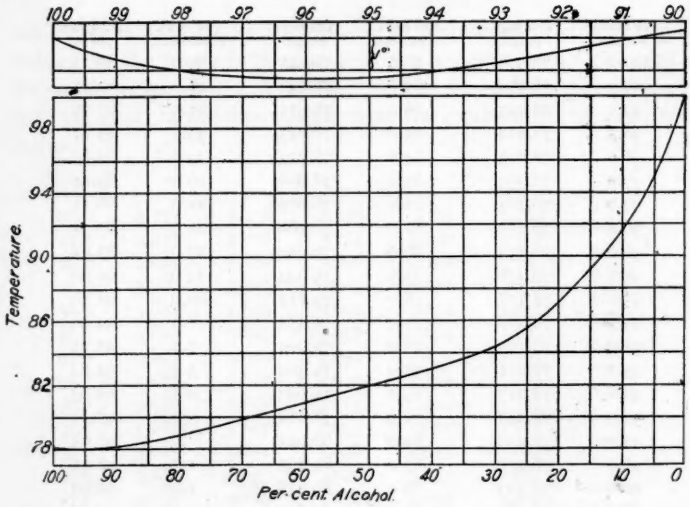
In the determination with small amounts of alcohol the readings of the thermometer were taken when the vapors first entered the condenser, as after boiling for a few minutes a relatively large proportion of the alcohol present would be found in the upper layers and in the condenser, and the thermometer under those conditions registered about 0.3 higher. It was shown by slow heating that the difference was not due to the lag of the thermometer.

An examination of the table and curve shows that the minimum boiling-point is for alcohol of 96 per cent. by weight. This corresponds to 97.45 per cent. by volume. Le Bel[1] gives the minimum as at 97 per cent. (presumably by volume, though he does not make this statement). His method would tend to place the minimum too low, unless moisture was very carefully excluded.

In the accompanying figure the upper part gives the boiling-point curve for alcohol of 90 to 100 per cent. on an enlarged scale. The lower portion of the figure gives the complete curve.

It will be seen that the curve is steeper on the side toward absolute alcohol than on the other side. Alcohol of 90.7 per cent. has the same boiling-point as absolute alcohol. An inspection of the curve also shows very clearly why it is easy to concentrate

[1] *Loc. cit.*



alcohol by distillation to a strength of 30 or 40 per cent. by weight, while the further concentration is relatively difficult.

ROSE POLYTECHNIC INSTITUTE,
TERRE HAUTE, June 1, 1901.

THE VOLUMETRIC DETERMINATION OF ZINC.

BY PERCY H. WALKER.

Received May 15, 1901.

THE most commonly used method for the determination of zinc is the volumetric process of titrating with standard potassium ferrocyanide, using either a uranium solution or one of cobalt nitrate or platinum chloride as indicator. The ferrocyanide titration has several disadvantages. The standard solution does not keep well, and hence must be frequently standardized. If too much ferrocyanide is added in titrating, there is nothing to do but make another determination. The method of using an indicator, by taking out drops, invariably introduces an error.

R. K. Meade[1] has given us a method based on an entirely different reaction. He precipitates the zinc as zinc ammonium arsenate, and uses this arsenate to liberate iodine, which is then titrated by thiosulphate.

The most satisfactory gravimetric process for determining zinc is the precipitation of zinc ammonium phosphate and weighing

[1] This Journal, **22**, 353 (1900).

as pyrophosphate, an analogous process being applied to manganese and magnesium.

Many years ago, Stolba[1] worked out an alkalimetric method for the determination of magnesium, by titrating the magnesium ammonium phosphate with standard acid. Handy's method[2] is a modification of Stolba's. This process may be much more easily used for the determination of zinc than for magnesium.

The process is carried out as follows: To the zinc solution, which should also contain ammonium chloride, a large excess of ammonia is added, then a large excess of sodium phosphate. The solution remains clear; but if the excess of ammonia is cautiously neutralized, a white cloud is formed as each drop of acid falls into the strong ammoniacal liquid. On stirring, this cloud dissolves until nearly all the ammonia is neutralized, when the whole solution becomes milky. It should now be heated to about 75° C. and stirred constantly, at the same time continuing the addition of dilute acid, drop by drop. In a very few minutes the precipitate becomes crystalline, and with care the liquid may be almost perfectly neutralized. It is a good plan to add a small piece of litmus paper to the liquid; this should not turn red but should remain blue or violet, while the hot liquid should have no odor, or only a very faint odor of ammonia. When the precipitation is made as above, the zinc ammonium phosphate is easily filtered, which may be safely done after five minutes' standing. The precipitate should be washed with cold water until the washings show only a faint trace of chlorides, then the paper with the precipitate returned to the beaker in which the precipitation was made, an excess of standard acid added, a few drops of methyl orange, and the exact point of neutrality determined with standard alkali.

According to the equation

$$ZnNH_4PO_4 + H_2SO_4 = ZnSO_4 + NH_4H_2PO_4,$$

we see that 1 cc. of normal acid corresponds to 32.7 mg. zinc. A solution of pure zinc oxide in hydrochloric acid was prepared for testing this method, the following results being obtained:

	Zinc taken. Gram.	Zinc found. Gram.
1	0.1490	0.1486
2	0.1490	0.1481
3	0.1490	0.1486

[1] *Chem. Centrbl.*, 1866, 727, 728; Sutton's "Volumetric Analysis," 6th ed., p. 87.
[2] This Journal, **22**, 31 (1900).

Since the zinc ammonium phosphate is not precipitated in presence of a large excess of ammonia, the process may be used in the presence of magnesium which is precipitated in the strongly alkaline liquid, and the filtrate from the precipitate neutralized to precipitate the zinc. About 1.15 grams of crystallized magnesium sulphate were added to some of the zinc solution, made strongly alkaline with ammonia, sodium phosphate added, and after standing about fifteen minutes with frequent stirring, filtered, washed, and the zinc determined in the filtrate.

Zinc taken.	Zinc found.
0.1490	0.1481

The process gives fairly good results in the presence of iron, calcium, and magnesium, as the following results will show. Where unknown but rather large quantities of solutions of iron (ferric), calcium, and magnesium salts were added to the zinc solution, the whole being strongly alkaline, sodium phosphate was added in large excess, the solution being in a graduated flask which was filled to the mark, mixed, filtered through dry paper and an aliquot part taken for determining the zinc.

Zinc taken. Gram.	Zinc found. Gram.
0.1192	0.1172
0.1192	0.1172

Manganese, however, must be previously separated, best by the nitric acid and potassium chlorate method.

UNIVERSITY OF ARKANSAS, May 8, 1901.

THE EXTRACTION OF MORPHINE WITH IMMISCIBLE SOLVENTS.

BY W. A. PUCKNER.

Received June 11, 1901.

A recent publication by F. Wirthle[1] relative to the extraction of morphine from its solution by means of a chloroform alcohol mixture leads me to publish some similar determinations. My experiments were made with a view of ascertaining whether instead of liberating the alkaloid by addition of fixed alkali there might be substituted ammonium hydroxide. This work was not completed on account of similar determinations published by Kippenberger[2]. While I did not find the substitution of ammonia ad-

[1] *Chem. Ztg.*, **25**, 291.

[2] *Ztschr. anal. Chem.*, **39**, 290.

10 cc. morphine solution (= 0.0998 gram alkaloid) was treated with	Shaken with 10, 10, and 10 cc. alcohol chloroform, the residue weighed. Gram.	Shaken with 10, 10, and 10 cc. alcohol chloroform, the residue the titration indicated. Gram.	Extracted with a fourth 10 cc. the residue weighed. Gram.	Extracted with a fifth 10 cc. the residue weighed. Gram.	Total morphine indicated by weight. Gram.	Total morphine indicated by titration. Gram.
a[3] 10 per cent. NH_4OH, 0.1 cc	0.0988	0.0967	0.0021	0.0010	0.1019	0.0986
a[4] 10 per cent. NH_4OH, 0.1 cc	0.0990	0.0983	0.0019	0.0008	0.1017	0.0992
c[2] 10 per cent. NH_4OH, 1.0 cc	0.0937	0.0910	0.0054	0.0013	0.1004	0.0980
c[3] 10 per cent. NH_4OH, 1.0 cc	0.0940	0.0919	0.0057	0.0016	0.1013	0.0986
c[4] 10 per cent. NH_4OH, 1.0 cc	0.0948	0.0922	0.0051	0.0014	0.1013	0.0995
e[1] NH_4OH, 1 cc., NH_4Cl, 3 grams	0.0989	0.0856	0.0051	0.0032	0.1073	0.0858
e[2] NH_4OH, 1 cc., NH_4Cl, 3 grams	0.0992	0.0847	0.0052	0.0031	0.1075	0.0850
f[1] 5 per cent. NaOH 0.2 cc	0.0440	.....	.....	.....	.....	.....
g[1] 5 per cent. NaOH 2.0 cc	0.0018	.....	.....	.....	.....	.....
h[1] 5 per cent. NaOH 0.2 cc. $NaHCO_3$, 1 gram	0.0853	0.0853	0.0147	0.0020	0.1020	0.1010
h[2] 5 per cent. NaOH 0.2 cc. $NaHCO_3$, 1 gram	0.0977	0.0952	0.0034	0.0013	0.1024	0.0989
h[3] 5 per cent. NaOH 0.2 cc. $NaHCO_3$, 1 gram	0.0991	0.971	0.0022	0.0003	0.1016	0.0992
i[1] NaOH 2 cc. $NaHCO_3$ 1 gram	0.0994	0.0974	0.0025	0.0003	0.1022	0.1001
i[2] NaOH 2 cc. $NaHCO_3$ 1 gram	0.0987	.....	0.0023	0.0003	0.1013	.....
j[1] NaOH 2 cc. NaCl, 2 grams	0.0092	.....	0.0071	0.0061	0.0224	.....
k[1] NH_4OH 1 cc., $NaHCO_3$, 1 gram	0.1008	0.0983	0.0008	0.0002	0.1018	0.0998
k[2] NH_4OH 1 cc., $NaHCO_3$, 1 gram	0.0997	.....	0.0008	0.0003	0.1008	.....

vantageous yet my results were more favorable than those of Wirthle and hence may be of some interest.

The morphine alkaloid used was purified by crystallization from hot absolute alcohol. Its purity, determined by titration with decinormal sulphuric acid and cochineal as indicator, was found to correspond to 99.50 per cent. monohydrated morphine ($C_{17}H_{19}NO_3.H_2O$). Of this, 2.5093 grams, corresponding to 2.4968 grams pure morphine, were dissolved in 10 cc. volumetric normal hydrochloric acid and sufficient water added to make 250 cc.

To extract and estimate the morphine in this solution 10 cc., representing 0.0998 gram morphine alkaloid, were in each case measured into a separatory funnel, rendered alkaline as below stated and then shaken with successive portions of a mixture composed of 80 volumes of chloroform and 20 volumes of alcohol. Three extractions of 10 cc. each were received in a shallow beaker (A). A further extraction of 10 cc. was received in a second beaker (B), and still another 10 cc. received in a third beaker (C). These liquids were allowed to evaporate spontaneously,[1] the residue kept over sulphuric acid for several hours, weighed, and then titrated with volumetric decinormal sulphuric acid, using cochineal as indicator.

These results show that while ammonium hydroxide combines with morphine to form a salt that is not readily taken up with the alcohol chloroform, it does so to a much smaller extent than sodium hydroxide. If as in *a* but a slight excess of ammonia is added, approximately 98 per cent. of the alkaloid is removed by the first three extractions. Even if ten times the amount used in *a* is added as in series *c* three extractions still remove more than 90 per cent., and practically all the alkaloid is obtained when five portions of the solvent are used. If a few drops of the cochineal indicator be added to the morphine solution and ammonia added to alkalinity the quantity used in *a* need not be exceeded. As might be expected the addition of sodium bicarbonate, *k*, overcomes the effect of an excess of ammonium hydroxide just as Kippenberger found this to be the case for fixed alkali. The

[1] If the evaporation is hastened by application of heat then a varnish-like residue is obtained from which the last traces of alcohol are expelled only with much difficulty. The residue left when the liquid has evaporated spontaneously is crystalline and loses no weight when dried at 60° C.; *i. e.*, morphine containing one molecule of water is thus obtained.

attempt to decrease the dissociation of the morphinate by ammonium chloride in *e* and thus permit its removal from the solution did not prove successful. The ammonium chloride apparently acts as so much free ammonia. The discrepancy in *e* between the weight of the residue and the morphine indicated by titration is due to ammonium chloride taken up by the solvent; to a moderate degree such disagreement is seen in all determinations.

UNIVERSITY OF ILLINOIS.

IMPROVED ELECTRIC FURNACE FOR LABORATORY USE.

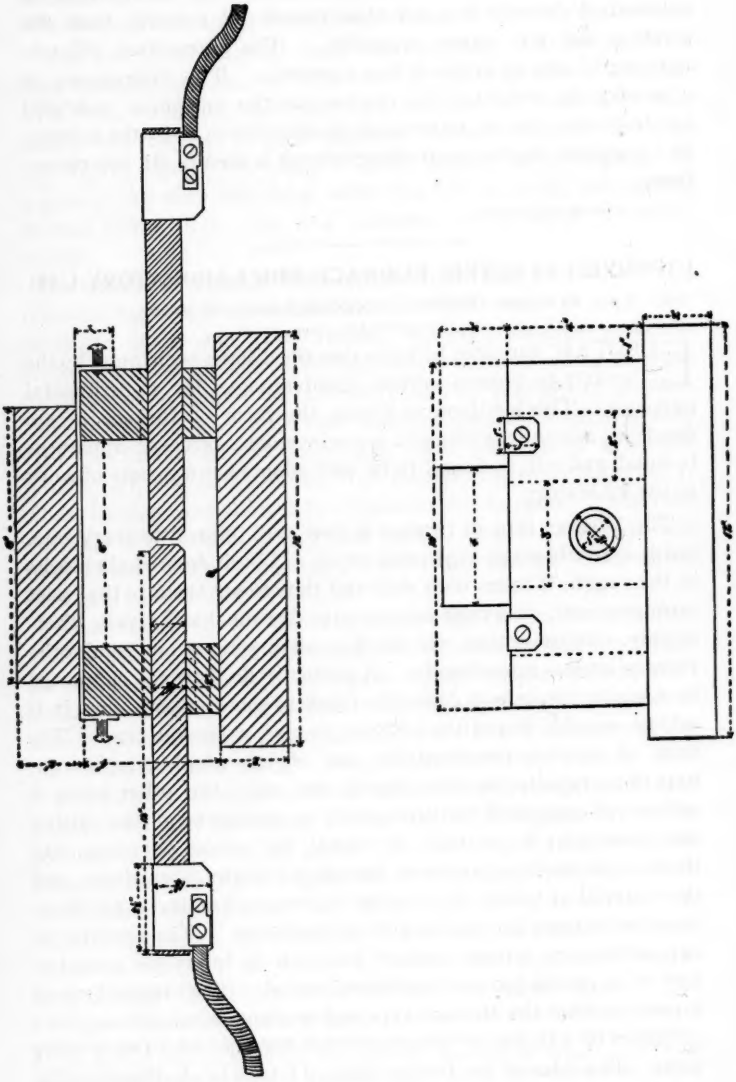
BY SAMUEL AUCHMUTY TUCKER AND HERBERT R. MOODY.

Received June 1, 1901.

ELECTRIC furnaces hitherto described have been found by the writers to possess certain disadvantages for experimental purposes. This led them to devise the form of furnace herein described which it is thought is a convenient piece of apparatus to build and will be found to be well adapted to a variety of work in the laboratory.

The Moissan type of furnace is now well known to every one, but it is troublesome in several ways. If built from chalk blocks in the rough, it takes both skill and time to cut them to the exact form required; it is then necessary to dry the blocks very thoroughly, otherwise they will crack in all directions and render the furnace useless immediately. A perfectly dry furnace supported by metallic bands will generally crack to some extent, and it is seldom possible to put the furnace in use a second time. The form of furnace described by one of us[1] which simply consists of a graphite crucible forming one pole, the other being a carbon rod supported vertically with an arrangement for raising and lowering it at will is useful for some purposes, but there is too much exposure to the air for many operations, and the material of which the crucible is composed is likely to introduce undesirable impurities during the fusion. The operator is exposed to very intense radiant heat which interferes considerably with its use for any lengthened period. The present form of furnace is after the Moissan type and is composed of carbon bricks 12 inches by 4 inches by 2 inches, luted together with Dixon stove paste. The sides of the furnace were of 6-inch brick, thus making

[1] *American Electrician*, 11, 408.



a working space of about 6 by 4 by 2 inches. This space could, of course, be increased or diminished at will according to the charge used. The whole was then clamped and held firmly together by iron cross bars provided with adjusting screws at each end, these bars being insulated from the body of the furnace by strips of asbestos. The end bricks were perforated with 1.5-inch holes containing a collar of asbestos or a small cylinder of clay, through which the electrodes of carbon passed (1 inch by 12 inches) into the furnace chamber. Connection was made with these electrodes by copper sleeves lined with copper gauze and tightened with set screws which at the same time carried copper lugs which held the flexible cables.

The tendency to overheat those portions of these electrodes outside of the furnace, and consequent wasting away, and also the tendency to melt the copper connections, was overcome by either one of two expedients; that is, by the use of the water-jacket or by heavily copper-plating the carbons. This latter did not furnish quite as perfect a protection, but it was somewhat less troublesome than the former, and was consequently the one most used.

The construction of this furnace gives it considerable durability; so much so is this the case, that only three sets of brick were used throughout the year in which almost a hundred runs were made. The greatest deterioration comes from the oxidation of the outer surface of the carbon bricks, and this could be largely avoided by a suitable covering of fire-bricks. Frequently ten or twelve runs could be made without dismantling the principal parts and the substitution of new asbestos collars serve to make everything ready for the next run.

In this type of furnace the desired current may be readily maintained throughout the entire fusion, and this is not easily done with a crucible furnace where variations are unknowingly introduced by the constantly changing distance between the poles. This form of furnace may be used with double arc on 110 volt circuit with considerable economy. For example, with a single arc furnace and with a polar separation of 18 mm. and enough resistance in circuit, the following reading was obtained: 125 amperes, 70 volts, and consequently 8,750 watts.

These should be compared with the following results obtained while using the double arc furnace. Here all the resistance was

cut out and then the instruments showed 175 amperes, and 90 volts. A few moments after this the reading was 125 amperes, and 100 volts or 12,500 watts.

The only difficulty in using this type is to prevent the extinction of the arcs, but that trouble is far from insurmountable. The dimensions given for the furnace are suitable for currents up to 300 amperes, at 70 volts. For work requiring more power than this it is necessary to increase the size throughout and use electrodes of 2-inch diameter.

If the luting has been carefully done the furnace will be sufficiently gas-tight to permit a fusion to be carried on in an atmosphere of any desired gas, the gas being introduced through an annular electrode. This furnace is adapted to almost all kinds of fusion processes, and has been used in the greatest variety of work.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED CHEMISTRY, UNIVERSITY OF MICHIGAN.]

THE OXIDATION OF NITROGEN AS A SOURCE OF ERROR IN THE ESTIMATION OF HYDROGEN AND METHANE.

BY ALFRED H. WHITE.

Received June 10, 1901.

THE author had occasion some time ago to estimate accurately a small amount of methane mixed with a large amount of hydrogen. A sample mixed with air was exploded in a Hempel pipette with due precautions to insure accuracy, the measurements being made in the author's burette for exact gas analysis previously described in this Journal.[1] Though great care was taken in the work, the results were so discrepant as to be entirely useless for the purpose. The results of a series of five experiments follow, arranged in the order of explosive ratios.

TABLE I.—EXPLOSION OF HYDROGEN AND A SMALL AMOUNT OF METHANE.

		After explosion.				
Gas sample. cc.	Air. cc.	Contraction. cc.	CO_2. cc.	Hydrogen. Per cent.	Methane. Per cent.	Explosive ratio.
12.87	103.24	16.97	0.05	87.64	0.39	5.77
13.79	86.89	18.39	0.04	88.51	0.29	5.08
13.17	84.18	17.56	0.06	88.27	0.45	4.54
14.77	87.23	19.66	0.09	87.92	0.62	4.20
18.38	87.03	24.48	0.16	87.62	0.87	3.30

The increasing amounts of carbon dioxide can not be laid to

[1] This Journal, **22**, 343.

diffusion through the potassium hydroxide used, for the pipette carried enough mercury in the bottom to form a trap, nor to solution of gas by the potassium hydroxide, for the pipette had been carefully saturated by a blank experiment, nor to leak in connections because in each case after removing the carbon dioxide by potassium hydroxide, and reading the volume, the gas was passed back into the same potassium hydroxide pipette, allowed to stand and again drawn back into the burette and the volume read. In only one case, the third given, did the variation in volume after such second treatment with potassium hydroxide amount to as much as 0.02 cc. In two other cases, the variation was 0.01 cc. and in the other two there was no change in volume. Leaving out of account the first of the series where it is probable the great dilution caused incomplete combustion, the other four results show increasing methane and decreasing hydrogen as the explosive ratio (ratio of the inert to the exploding gas) grows smaller. The decrease in the percentage of hydrogen results from the method of calculation, all the contraction over potassium hydroxide being considered as carbon dioxide, and calculated to methane. The increase in the apparent carbon dioxide points strongly to the formation of oxides of nitrogen. That these are formed and may cause error in explosion analyses was shown long ago by Bunsen, who experimentally determined certain limits within which there was no appreciable error. The explosive ratio for pure hydrogen, according to Bunsen, might safely vary from 3.81 to 1.55. He did not determine whether any gases absorbable in potassium hydroxide were formed in the explosion. The results above cited have, with one exception, higher explosive ratios than his highest, and yet there is apparently considerable formation of an oxide of nitrogen which is absorbed by potassium hydroxide.

Bunsen's results have been seemingly everywhere accepted without question. Hempel, in the 1900 edition of his "Gasometrische Methoden," quotes Bunsen's results[1] with the comment that "by keeping to the Bunsen norm the worst that may happen is that the mixture is not explosive. The combustion of nitrogen will certainly be avoided."

The marked disagreement of the results given by Bunsen and those of Table I made it desirable to make a series of experiments

[1] Hempel: "Gasometrische Methoden," 3te Auflage, p. 113.

on pure hydrogen. The hydrogen was generated by the action of potassium hydroxide on aluminum in order to obtain it free from the small amounts of hydrocarbons usually present in gas obtained by the action of an acid on a metal. The results are given in Table II.

TABLE II.—EXPLOSION OF PURE HYDROGEN.

Sample hydrogen. cc.	Air. cc.	Contraction after explosion.	Hydrogen. Per cent.	Contraction over potassium hydroxide.	Explosive ratio.	Bunsen's results recalculated. Explosive ratio.	Bunsen's results recalculated. Hydrogen. Per cent.
11.35	84.80	16.90	99.26	0.00	4.64	3.81	99.92
12.11	85.57	18.08	99.53	0.00	4.37	2.90	99.56
14.19	84.27	21.27	99.92	0.00	3.62	2.29	99.84
16.77	85.77	25.13	99.90	0.01	3.06	1.95	100.04
16.54	82.64	24.76	99.80	0.01	3.00	1.55	100.15
18.19	83.22	27.29	100.01	0.01	2.71	1.25	100.72
21.10	83.28	31.74	100.28	0.00	2.29	1.04	103.14
27.04	83.86	40.80	100.59	0.11	1.73	0.37	105.06

Bunsen's results recalculated to permit direct comparison are appended. Bunsen held that the explosive ratio might vary from 3.81 to 1.55 without causing appreciable error, though the smaller ratio gives erroneous results according to his own figures.

These figures for the explosion of pure hydrogen in Table II do not show as great variations with change of explosive ratio as do the results in Table I of explosion of a gas carrying a small amount of methane mixed with a large amount of hydrogen. To determine if the methane caused the difference, a series of explosions of methane and air were made. The methane was made from methyl iodide and the zinc copper couple, and both gas and air were freed from carbon dioxide before use. Table III gives the results of this series.

TABLE III.—EXPLOSION OF METHANE.

Sample methane. cc.	Air. cc.	Contraction after explosion.	Carbon dioxide cc.	Methane. Per cent.	Hydrogen. Per cent.	Explosive ratio.	Ratio contraction / sample
7.05	92.07	13.09	6.53	92.62	0.28	4.05	1.85
8.93	104.17	16.66	8.31	93.28	0.14	3.53	1.86
9.07	98.35	17.10	8.54	94.15	0.14	3.19	1.88
10.20	98.22	19.27	9.63	94.41	0.06	2.61	1.89

In these experiments the explosive ratios all lie within Bunsen's limits for methane of 4–2.7; still there is a variation of 1.6 per cent. in the apparent percentage of methane as calculated by the usual methods and a corresponding variation in the amount

of hydrogen. The precautions mentioned before were taken to prevent error from diffusion or solution in the potassium hydroxide pipette. In all these experiments the gases had been diluted with air and the preponderating inert gas was nitrogen. Several experiments were made with mixtures of hydrogen and methane to determine whether any more trustworthy results might be obtained, using oxygen alone in excess. The oxygen gas used was 96.5 per cent. pure. The results showed that the errors when using oxygen thus were rather greater than when using air in similar amount. In several cases, both when using oxygen and air, Griess' reagent for nitrites (naphthylamine hydrochloride and sulphanilic acid) was introduced into the pipette before explosion, with the result that a deep red color was always formed after explosion, proving the formation of nitrous acid.

The explanation of the discrepancies between the author's work and Bunsen's is probably to be sought for in the different forms of apparatus employed. Bunsen used a narrow eudiometer in which the propagation of the explosion and liberation of heat would be slower and the absorption of heat by the glass walls more rapid than in the nearly spherical Hempel pipette; hence the temperature of combustion would be less in Bunsen's work and there would be a smaller amount of oxides of nitrogen formed. In Bunsen's eudiometer also explosion took place under diminished pressure, while in the Hempel apparatus a considerable plus pressure was generated in the explosion. It follows that when working with the Hempel apparatus a greater amount of inert gas than Bunsen found necessary should be present. Apparently the most nearly correct results are obtained in the case of hydrogen when the ratio of the non-explosive to the explosive gases follows Bunsen's higher figure; *i. e.*, when the explosive ratio varies from 4 to 3. In no case will absolutely correct results be obtained, as probably in all cases of explosion under these conditions nitrogen is oxidized to some extent. In the case of methane the higher temperature of combustion causes greater errors and here also the higher explosive ratio given by Bunsen should be adhered to.

The method of Dennis and Hopkins,[1] in which the gas in contact with a glowing platinum spiral burns quietly in a current of

[1] This Journal, **21**, 398.

oxygen and air, allows the use of a larger sample. It is moreover indorsed by Hempel in the following words:[1] "The advantage gained is that in the beginning, where the combustion might become too intense, there is always an excess of combustible gas, so that on the one hand no explosion can take place, and on the other none of the nitrogen can burn, as the combustion takes place at the beginning with an insufficient amount of oxygen, and towards the end when the combustion becomes complete, such high temperatures as are necessary for the combustion of nitrogen are not reached at all."

Some preliminary experiments having shown that it was by no means so certain that nitrogen might not burn under these conditions, tests were made on air with Griess' reagent for nitrites in the pipette, when it was found that a test for nitrites quickly developed after heating the wire. Table IV shows quantitatively the effect on the volume of air when the spiral is heated to redness. The air was freed from carbon dioxide and the samples were as nearly as might be 80 cc. each. While it was not possible to measure accurately the temperature of the wire, a comparison could be obtained by measuring the current heating it. A current of 4 amperes heated the wire to barely visible redness in the daylight and 5.35 amperes heated it to a white heat. The time was in each case two minutes.

TABLE IV.—EFFECT OF HEATING PLATINUM SPIRAL IN AIR.

Sample air. cc.	Current amperes.	Contraction after heating. cc.	Contraction after potassium hydroxide. cc.	Total contraction. cc.
80.90	4.0	0.01	0.00	0.01
82.51	4.55	0.04	0.02	0.06
80.99	4.6	0.03	0.03	0.06
81.22	4.65	0.04	0.01	0.05
81.70	4.8	0.04	0.10	0.14
81.88	5.0	0.11	0.10	0.21
83.10	5.1	0.08	0.17	0.25
80.49	5.3	0.06	0.18	0.24
80.67	5.35	0.12	0.18	0.30

It will be observed that the sum of the contraction after heating and after potassium hydroxide given in the last column increases quite regularly with increase in temperature, but that there is considerable irregularity in the ratios between the contraction after heating and the contraction after potassium hydroxide. It

[1] "Gasometrische Methoden," 3te Aufl., p. 123–124.

may be that the more or less complete condensation of the nitric acid formed, depending upon time, contact, and the amount of water present, is sufficient to account for it.

To afford a direct comparison between the explosion and combustion method, hydrogen generated from aluminum and caustic potash was stored in a gas-holder containing mercury and a little dilute caustic potash. The hydrogen was supposed to be pure but evidently contained a little air. The oxygen used was about 97 per cent. pure.

TABLE V.—COMPARISON OF EXPLOSION AND COMBUSTION METHODS ON HYDROGEN.

Explosions with Air.

Sample hydrogen. cc.	Air. cc.	Contraction after explosion. cc.	Contraction over potassium hydroxide. cc.	Hydrogen. Per cent.	Explosive ratio.
15.32	85.34	22.71	0.04	98.82	3.43
18.15	82.39	26.93	0.06	98.91	2.73

Explosions with Oxygen.

	Oxygen.				
14.82	93.51	22.04	0.02	99.14	3.91
16.48	82.18	24.51	0.02	99.15	3.02
20.58	80.09	30.60	0.03	99.12	2.29

Combustions by the Dennis and Hopkins Method.

	Oxygen.	Air.				Oxygen in excess.
91.29	51.65	54.55	136.72	0.04	99.84	13.72
58.48	53.39	50.14	87.43	0.10	99.66	40.89
89.31	40.77	50.21	133.57	0.07	99.70	3.73

The results of the explosions with oxygen are slightly higher than those with air, show very little contraction over potassium hydroxide, and remarkably little variation with change in explosive ratio. The results with the Dennis and Hopkins method are about 0.6 per cent. higher than those obtained by explosion with oxygen. The variations in the individual results by this method may easily be accounted for by the intentional variation in the proportions of nitrogen and oxygen used, and the unavoidable differences in temperature of spiral and time of heating.

The question naturally arises, which of these methods is more reliable. That none of them are entirely correct is certain, for if nitrogen of the air is oxidized to an appreciable extent by a platinum spiral heated to dull redness, oxides of nitrogen must be formed in all combustions. This has been shown by Ilosvay[1] for

[1] *Bull. Soc. Chim.*, **11**, 737 (1889).

flames, even when the temperature of combustion was much reduced by dilution of the gas with carbon dioxide. The same author also found a slight formation of nitrous acid in the case of air burning in an atmosphere of illuminating gas, where a reducing atmosphere would always be present.

SUMMARY.

Oxides of nitrogen are always formed in explosion analysis in amount increasing with the violence of the explosion. The dilution recommended by Bunsen, when exploding in eudiometer tubes under reduced pressure, is not sufficient when working with the Hempel explosion pipette. If the explosive ratio is kept between four and three, the error is negligible in the technical analysis of gases almost entirely hydrogen. The presence of small amounts of methane increases the error and if large amounts of methane are present, the error may easily amount to a per cent. or more. The explosive ratio should be kept between four and three as in the case of hydrogen. The method of Dennis and Hopkins tends to give high results, and the errors may easily become of importance if care is not taken to avoid heating the spiral too hot and too long. Neither the explosion method nor any method involving active combustion can give strictly accurate results.

ANN ARBOR, MICHIGAN,
June, 1901.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE.]

NOTE ON SOME MODIFIED FORMS OF PHYSICO-CHEMICAL MEASURING APPARATUS.

BY ALLERTON S. CUSHMAN.

Received May 21, 1901.

a. A CONVENIENT ARRANGEMENT OF THE KOHLRAUSCH-OSTWALD CONDUCTIVITY CELL.

IN working with the usual form of Kohlrausch-Ostwald conductivity cell the writer has experienced some difficulty in arranging the electrodes so that they may be easily adjusted at any required distance one from the other, while on the other hand, when once set to a position the constant for the cell may be depended upon. The growth of physico-chemical methods of investigation has been so sudden that the manufacturers of instruments of precision have not kept pace with the requirements of

modern research. The physical chemist therefore has been obliged to depend largely on "home-made," and too often very imperfect, apparatus. It is not uncommon in many laboratories to see this important and delicate measuring instrument arranged in such a way that the electrodes are most insecurely fastened into place by means of splashes of sealing-wax, or, as is the case with the cells ordinarily supplied by the dealers, the mere friction of the glass supports of the electrodes against the holes in the ebonite cover through which they pass, is depended upon to insure the constancy of the cell.

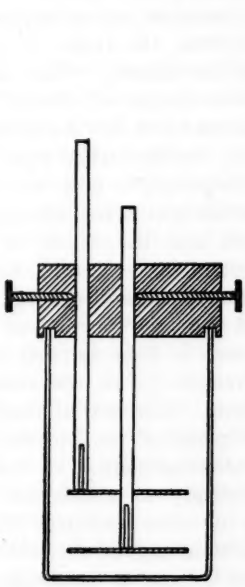


Fig. 1.

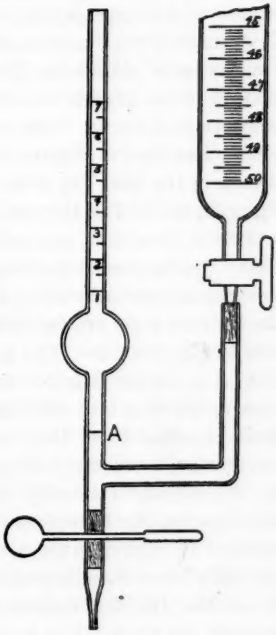


Fig. 2.

In Fig. 1 of the accompanying illustration is shown an arrangement of the cell which very admirably meets every requirement. The glass tubes into which the electrodes are fused, fit snugly, but without binding, the holes in the heavy ebonite cover, which is in cross-section in the cut. The brass set-screws as shown are

furnished with ebonite tips, which bear gently on the glass supports and remove the danger of contamination of the electrolyte by any accidental wetting of the screw points. A cell of this description which has been in frequent use for more than a year has not changed its constant. The electrodes are made of platinum, of nearly a millimeter in thickness and are secured to the glass supports with such care that they are quite immovable.

b. ON A MODIFIED FORM OF THE OSTWALD BURETTE-CALIBRATOR.

The usual Ostwald burette-calibrator has the general form shown in Fig. 2, without the etched scale upon the pipette stem. It is calibrated to deliver exactly 2 cc. between two etched marks and the deviations of the burette scale from the truth are then found by a series of deliveries from the pipette. The initial standardization of the pipette requires a number of careful and difficult weighings of water. In order to avoid this standardization the writer has used a pipette with a scale etched upon the stem as shown in the cut. It is only necessary to take care that when the pipette is filled to the etched mark at A that about 2 cc. more will put the meniscus somewhere near the middle of the pipette scale. Starting with the burette filled to the zero reading and the lower meniscus coinciding with the mark at A, the first 2 cc. of the burette scale are delivered into the pipette and the pipette-scale reading noted. The pipette is then emptied to A and the next 2 cc. of the burette delivered. This operation is repeated down the length of the burette. One set of readings can be made starting from the zero point of the burette and another set starting from the 1 cc. graduation mark. In order to apply the corrections it is only necessary to standardize the pipette scale against the burette scale by a few fractional fillings of the pipette. In applying the corrections any of the ordinary methods of calibration may be employed, such as assuming the first 2 cc. of the burette correct, and, then distributing the deviations from the truth. For most laboratory work exceedingly small deviations are negligible, but the fact that a serious deviation from the truth may introduce a constant error into a series of observations, makes a rapid and easy method of becoming acquainted with the variations of burette scales of great value. This instrument permits this to be done with but little expenditure of time and without the necessity of making a single weigh-

ing. Bad burettes can be immediately condemned and those of sufficient accuracy for the work in hand selected. In case absolute corrections are demanded the pipette can be standardized by the method of weighing much more easily than one that is not provided with an etched scale on the pipette stem. Of course the pipette must be made scrupulously clean with a chromic-sulphuric acid mixture before it is used.

May 20, 1901.

A RAPID METHOD FOR THE DETERMINATION OF ARSENIOUS OXIDE IN PARIS GREEN.

By S. Avery and H. T. Beans.

Received May 17, 1901.

THE authors have been working for some time on a method for determining the arsenic in Paris green, in the hope that one might be found that would be both more rapid and accurate than any thus far proposed. As a result we offer the following method, which we believe to be new and which has given most excellent results on a considerable number of samples of Paris green examined in this laboratory.

For the determination, sample the Paris green by quartering (as one would an ore for assaying) down to about 1 gram. Pulverize this small sample in an agate mortar and weigh out 0.2 to 0.3 gram into a beaker of about 300 cc. capacity. Add about 25 cc. of water and to the green suspended in water add, with constant stirring, concentrated hydrochloric acid till solution is just effected; from 6 to 10 drops are usually sufficient. Now add to the acid solution sodium carbonate solution till a slight permanent precipitate is formed, and at this point add 2 to 3 grams of sodium potassium tartrate in solution. The tartrate will at once dissolve the precipitated copper and prevent further precipitation during the subsequent titration. Dilute to about 200 cc., add solid sodium bicarbonate and starch solution, and titrate with iodine in the usual way.

The time required for the determination is about ten minutes. The end reaction is sharp and is not in the least obscured by the blue color of the copper solution.

Triplicate determinations on the same sample of a very uniform Paris green were as follows, taking 0.3 gram Paris green for analysis.

Iodine solution. cc.	As_2O_3. Gram.	As_2O_3. Per cent.
34.52	0.17056	56.85
34.59	0.17091	56.97
34.58	0.17086	56.95

To make sure that the presence of copper exerted no influence, several lots of pure arsenious oxide were weighed out. Some of these were titrated as usual and the others were first mixed with about an equal weight of copper sulphate in solution and then with the tartrate according to the method given. No appreciable difference could be observed in the several titrations.

Several other analysts, as well as ourselves, have found that the results, in terms of metallic arsenic, obtained by this method are slightly higher than the results by other methods, even when the latter admit of the determination of arsenic in either stage of oxidation. This fact would seem to indicate that the Paris greens on the market contain arsenic in the lower stage of oxidation only.

Cuprous oxide interferes with the titration, but we have not observed the presence of copper, in this degree of oxidation, in any of the samples examined. It is, of course, possible that adulterants might be added that would affect iodine or iodine salts, but such samples have not as yet been met with, to our knowledge.

In conclusion we would express our obligations to Dr. H. W. Wiley for his kindness in having the literature of the subject thoroughly searched for our guidance.

CHEMICAL LABORATORY, UNIVERSITY OF IDAHO.

NOTE ON THE ANALYSIS OF NUCLEIC ACIDS OBTAINED FROM DIFFERENT SOURCES.

BY P. A. LEVENE.

Received May 18, 1901.

THE author has repeated the results of the analysis of several nucleic and paranucleic acids obtained by a method communicated by him at a previous meeting of the Society.

The paranucleic acids analyzed were those of vitellin and of the ichtulin of the cod-fish egg. Their composition was as follows:

	Vitellinic acid.	Ichtulinic acid.
Carbon	32.31	32.56
Hydrogen	5.58	6.00
Nitrogen	13.13	14.00
Phosphorus	9.88	10.34

Thus these "paranucleic" acids of different origin have a comparatively similar composition. The difference in the nitrogen is easily explained by the fact that the ichtulinic acid was obtained from the ammonium salt, and the vitellinic from the copper salt. If the latter acid is obtained from the ammonium salt it also contains about 14 per cent. of nitrogen.

The nucleic acids analyzed were those of the pancreas of the cod-fish and fish sperm, and of the Bacillus tuberculosis.

Their composition was as follows:

	Pancreas.	Cod-fish sperm.	Bacillus tuberculosis.
Carbon	36.50	36.73	38.78
Hydrogen	4.69	5.12	6.32
Nitrogen	16.70	16.78	9.42
Phosphorus pentoxide	20.16	20.47	29.40

The acid obtained from the pancreas in distinction from the guanilic acid described by Bang contains in its molecule besides guanin also adenin. This acid as well as that of the cod-fish sperm does not differ much in its composition from the acids described within the last year by Schmideberg, Herlant, Osborne, and obtained from different sources.

The author also remarked that on precipitating the nucleic acids directly from tissues glycogen is precipitated simultaneously. The two can be separated by means of copper chloride. The nucleic acid forms a copper salt insoluble in water, while the copper compound of glycogen is soluble. By this method the author succeeded in obtaining glycogen from the pancreas, and a glycogen-like substance from the Bacillus tuberculosis.

ON THE ELIMINATION AND QUANTITATIVE ESTIMATION OF WATER IN OILS, FATS, AND WAXES.

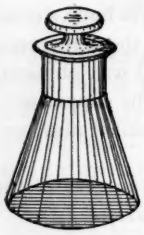
By Charles B. Davis.

Received March 19, 1901.

THE difficulty experienced while drying oils, fats, or waxes, (namely, loss by foaming and ejection, due to the contained water becoming overheated, as in the drying of the min-

eral oil residue obtained after removal of the fatty oil by saponification, in the analysis of lubricants) can be very readily obviated by the following method:

Into a wide-mouthed glass-stoppered weighing-bottle (see figure), is introduced sufficient thick filter-paper[1] (in coil form) to half fill the vessel. The bottle and paper are now dried in the air-oven at 110° C. to constant weight.



A portion of the sample is then added, in such quantity as will just saturate the filter-paper. The bottle being now closed and reweighed, the increase in weight gives the quantity of sample taken. The whole is now placed in the air-oven at 110° C.,[2] and dried to constant weight. The decrease thus obtained, gives the water evaporated, which may be calculated to percentage from the data obtained above. Samples prone to oxidation are dried in an atmosphere of CO_2 or H_2.

In treating oils containing water, or where the whole of the residue is to be dried and the oil only determined, or the water simply eliminated, the sample is completely transferred to the tared bottle containing the dry filter-paper by means of ether, the ether removed by evaporation at slightly elevated temperature, after which it is dried in the air-oven as above described.

Solid fats and waxes are introduced into the weighing bottle prepared as above, in their natural state, which, upon being warmed to the temperature of the oven, are quickly absorbed by the filter-paper, and drying proceeded with as in the case of liquids.[3]

By the above method, all foaming and ejection of the sample is eliminated, due to the fact that the oil, fat, or wax, and the water are thoroughly distributed throughout the paper while the drying operation is carried on.

A typical example of the value of the above method may be readily seen, and appreciated by referring to T. B. Stillman's "Engineering Chemistry," p. 368, in which he condemns the drying of oils containing water on account of this loss by foaming and ejection.

[1] Asbestos is not recommended on account of its property of retaining water even at 110° C. (this Journal, **22**, 46).

[2] Or at temperature other than 110° C., in any case, the bottle, plus paper, is to be dried in the beginning at the same temperature.

[3] If oil, fat, or wax be required for further examination, it may be removed from the paper by ether extraction in a Soxhlet apparatus.

ON THE DECOMPOSITION OF SODIUM NITRATE BY SULPHURIC ACID, II.

By C. W. Volney.

Received May 24, 1901.

On a former occasion[1] I presented to this Society a report on my work under the same title. The previous work had reference mainly to the conditions under which nitric acid distilled from a mixture of sodium nitrate and sulphuric acid.

Professor Lunge, in the second edition of his handbook "Sulphuric Acid and Alkali,"[2] quotes from the above cited article; but the process of decomposition in the said work, is still represented as $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$. I now report results of further investigation of this process. In the first part of the report already referred to, I have called attention to the strength of the nitric acid, which distilled at certain fixed temperatures, and I concluded, from the boiling-points, the temperatures of the residues in the retort, and the quality of the acid obtained, that during the second period all nitric acid had distilled off, and that only a disulphate was left in the retort.

I have since gone over the work again, and considered not only the distilled acid, but also the residues in the retort, which remain after each period of distillation. For this reexamination I used, for each period of distillation, a fresh quantity of nitrate and sulphuric acid, interrupting each process after the distillation of acid had entirely ceased, at the temperatures given. For each test, 500 grams sodium nitrate and 550 grams sulphuric acid were used; the results obtained were in agreement with those already described, as far as the strength of nitric acid is concerned. I have, at several times, attempted to separate the liquid from the solid portions of the salt cake. It is quite easy to separate the liquid from undecomposed nitrate by pouring the hot mass off. This must be done when the mass is still quite hot, as on cooling it will readily crystallize.

The distillation of nitric acid below 100° was carried out by heating in a liter retort, 500 grams sodium nitrate and 550 grams sulphuric acid at a temperature of 130° in the oil-bath, and keeping as near that temperature as possible, for thirty-six hours.

[1] This Journal, 13, 246.

[2] Edition of 1893, p. 116.

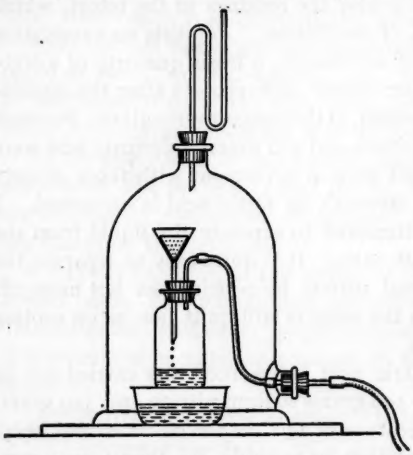
No further distillation could then be perceived. The residue in the retort consisted of unchanged nitrate and thick oily liquid. It was poured into a hot porcelain dish, which had been placed in an oil-bath of 100°, and from the hot mass a sufficient quantity of oily liquid was removed into another porcelain dish, where, on cooling, the liquid formed a crystalline salt in minute elongated prisms. The crystalline mass thus obtained, was left in a vacuum of 100 mm. at the ordinary temperature, for forty-eight hours, over sulphuric acid, and as it had lost nothing in weight, the sodium and sulphuric acid were determined, and gave the following results:

	Per cent.	Per cent.	Per cent.	Per cent.
Na	8.91	9.3	9.06	8.78
SO_4	90.0	90.9	87.75	85.1

which gives on the average for this salt:

	Per cent.
Na	9.01
SO_4	88.44

These results were obtained by the analysis of crystals furnished by solidifying the oily liquid above mentioned. As it is rather difficult to exclude the moisture of the air during the crystallization, and as thereby the crystals are destroyed, I have separated the solution from the solid residues in the retort, and then also from any possible excess of sulphuric acid, by filtration in vacuum, whereby the atmospheric air is almost totally excluded.



The simple apparatus is illustrated in the accompanying cut, and I may state here, also, that I arrived at the described construction of the apparatus after trying to obtain pure crystals by centrifugal filtration and vacuum filtration in a Gooch cru-

cible; but I prefer at present, the following apparatus: the glass funnel contains a filter of platinum, finely perforated, and it can be seen that only the air in the bell-jar, which is dried over sulphuric acid, can come in contact with the substance on the platinum filter. Under a vacuum of 650 mm. the solution of salts in sulphuric acid is quickly removed from crystals remaining on the platinum, and any absorption of moisture is excluded. The average of three determinations gave

Na	9.476
SO_4	89.094

The sodium was determined as neutral sodium sulphate, and the sulphuric acid as barium sulphate. Comparing these with the composition of sodium trisulphate, $NaH_3(SO_4)_2$, we have the following:

	Calculated.	Found.
Na	10.550	9.362
SO_4	88.07	89.147
H_3	1.38	1.491
	100.000	100.000

The figures seem to be sufficiently close to the theoretical, to justify the conclusion, that during the first period of the action of sulphuric acid on sodium nitrate, the above indicated trisulphate is formed, provided that the temperature of the contents of the retort does not go above 100°. At this period then, the residue in the retort consists of the remaining sodium nitrate and sodium trisulphate. The process that has taken place, may therefore, be expressed by

$$NaNO_3 + 2H_2SO_4 = NaH_3(SO_4)_2 + HNO_3,$$

and if the temperature is not raised above 100°, no further action of sulphuric acid on sodium nitrate can be perceived.

The second period of acid distillation ends at a temperature of 121°. For the investigation of this period, 500 grams sodium nitrate and 550 grams sulphuric acid were distilled in the same manner as before, but the temperature, after the first period of about 100°, was raised in the oil-bath to 165° and kept so, until all trace of acid, distilling at 121°–122°, had disappeared from the residue.

This was again poured hot into the heated porcelain dish, parts of the liquid cooled to crystallization, crystals dried in a desiccator over calcined potash at about 100 mm. pressure and finally sodium and sulphuric acid determined.

The figures obtained in these determinations are rather irregular; they gave as an average

	Per cent.
Na	18.730
SO_4	81.310

and compare with the acid sulphate of sodium thus:

	Calculated.	Found.
Na	19.166	18.730
SO_4	80.000	81.310
H	0.834	.....
	100.000	100.040

It is probable, that at the end of this phase some of the trisulphate, $NaH_3(SO_4)_2$, was still left in the residue; but it seems reasonable to assume the existence of $NaHSO_4$ in the salt cake, which now remains in the retorts.

The conclusions, which may safely be drawn from this work, are:

During the first period of action of sulphuric acid on sodium nitrate, polysulphate of the composition $NaH_3(SO_4)_2$ is formed, thus:

$$NaNO_3 + 2H_2SO_4 = NaH_3(SO_4)_2 + HNO_3.$$

The nitric acid, thus set free, is the true first hydrate and it distils over at its boiling-point between 81° and 88°.

The residue in the retort consists of trisulphate and nitrate, still undecomposed. On raising the temperature, the second phase of the process begins; the trisulphate acts at the higher temperature on the remaining nitrate

$$NaH_3(SO_4)_2 + NaNO_3 = (NaHSO_4)_2 + HNO_3,$$

and if this is carried out to the finish, the residue in the retort will consist entirely of $NaHSO_4$; and the acid distilling should also be HNO_3.

At the beginning of the distillation, free sulphuric acid is acting on a part only of the nitrate at a low temperature, at which the first hydrate distils undecomposed; during the second period, the action of the trisulphate on the remaining sodium nitrate requires a higher temperature, at which nitric acid of the composition HNO_3 begins to decompose, and H_2O is always formed from HNO_3. The acid distilling during the period is, therefore, of a different concentration and is sometimes called the second hydrate. This investigation will be continued.

NEW YORK, December 20, 1900.

MODIFIED WILLIAMS METHOD FOR MANGANESE.

By Randolph Bolling.

Received June 21, 1901.

THE Williams method, as outlined in Blair's "Chemical Analysis of Iron," although a very accurate one, is unsatisfactory on account of the time required for the filtration of the precipitated manganese dioxide, which, together with a frequently occurring mass of gelatinous silica, chokes up the asbestos filter and makes the operation more or less tedious.

The following modification has been found to overcome this difficulty entirely, and its adoption has reduced the time of a determination very materially, by eliminating the uncertainty attendant upon the filtration of the slimy manganese dioxide.

METHOD.

Place 5 grams of pig-iron drillings in a No. 5 Griffin's beaker, with cover glass, add 75 cc. nitric acid (sp. gr. 1.20), and after violent action has ceased add approximately 10 cc. hydrofluoric acid. Give the beaker a circular motion to mix contents, and evaporate down until ferric oxide begins to separate out. Cool, add 100 cc. nitric acid (sp. gr. 1.42), and heat to boiling. Drop in a spoonful of asbestos fibers and then add approximately 7 grams potassium chlorate. Boil until green fumes disappear and nitric acid begins to volatilize. Remove from source of heat, cool rapidly, and filter the manganese dioxide precipitated on the suspended asbestos fibers, on a special filtering tube. Wash twice with strong nitric acid, and rinse out the beaker in which the precipitation was made with cold water, pouring the rinsings through the filter-tube. Continue the rinsing and washing until, when tested with litmus, no acidity is shown. Push the asbestos pad and precipitate back into the beaker, wash down the sides of the filter-tube to remove all adherent manganese dioxide, and run in 50 cc. acid ferrous sulphate solution. Disintegrate the asbestos fibers with a stirring rod, and after the precipitate is entirely dissolved, titrate with permanganate. The filtering tube is prepared by taking a glass tube thin enough to slide loosely down the stem of a carbon funnel, heating one end until it balls and then pressing out flat. By softening the edge of the flat end and pressing a nail against the circumference at regular intervals the disk can be made fluted. Slip this rod in a carbon funnel, pushing down

until the disk rests solidly, place on it a little dry asbestos, and then pour on it asbestos suspended in water, using a moderate suction to make the pad fairly compact.

ACID FERROUS SULPHATE.

Dissolve 20 grams chemically pure ferrous sulphate in water, add 200 cc. strong sulphuric acid, and dilute to 2 liters.

POTASSIUM PERMANGANATE SOLUTION.

The strength of this solution should be such that 1 cc. equals about 0.0056 gram iron.

STANDARDIZATION AND CALCULATION OF RESULTS.

To standardize both the ferrous sulphate and the permanganate at the same time, take an iron in which the manganese has been accurately determined and treat it according to the method given until the precipitate of manganese dioxide is obtained. Dissolve the precipitate in 50 cc. of ferrous sulphate solution and titrate with permanganate, then run in 50 cc. additional of the ferrous sulphate and titrate again, to obtain the amount of permanganate necessary to oxidize 50 cc. of the ferrous sulphate solution. By deducting the number of cubic centimeters used in the first titration from the number used in the second, we obtain the volume of solution oxidized by the manganese dioxide. Dividing the percentage of manganese in the sample by the figure thus obtained and multiplying this by the number of grams of the original sample, we obtain the value of 1 cc. permanganate in terms of manganese. For instance, if we take 5 grams of a pig iron containing 1.13 per cent. manganese and use 4.6 cc. permanganate in the first titration, and 20.8 cc. in the second titration, then the difference of 16.2 cc. is the measure of the amount of ferrous sulphate oxidized by the manganese dioxide. Dividing 1.13 by this 16.2 and multiplying this by 5 we obtain the value of 1 cc. or 0.0034 gram manganese. The object of standardizing in this way, is to carry out the process under conditions similar to those which occur in a regular determination, for the results obtained by titrating clear ferrous sulphate are always lower than when carbon and asbestos are in the solution, for the reason that the eye of the observer notices the rose tint at once in a transparent solution, but the sharpness of the end reaction is slightly obscured by asbestos and carbon, hence the operator runs

a little past the true point. So that if both titrations are made under like conditions this error is completely eliminated.

The calculations in a determination are made thus: If 5 grams of the sample are taken, 50 cc. ferrous sulphate equals 20.8 cc. permanganate; 1 cc. permanganate equals 0.0034 manganese; 6.2 cc. are required to oxidize the ferrous sulphate not oxidized by the manganese dioxide.

$$\text{Then } \frac{(20.8 - 6.2) \times 0.0034 \times 100}{5} = \text{per cent. manganese.}$$

The time saved by the suspension of the manganese dioxide, and the elimination of silica in the filtering of the manganese dioxide, makes it possible to make a determination in about one hour. The method of standardizing solutions is not based on the reaction that is given in the text-books which is

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O,$$

as it was found that solutions standardized on the above reaction were invariably too low in their manganese value. This may be accounted for in the composition of the precipitate, for it is possible that MnO, Mn_2O_3, Mn_3O_4, Mn_5O_7, may be formed in part. At any rate, if we adopt the MnO_2 theory and standardize accordingly, the method will not give the same result on a sample that has the manganese determined by the basic acetate separation and the manganese weighed as manganese pyrophosphate according to Gibbs. On this account it is preferable to use a standardized sample of pig iron.

Below are given some determinations on ores and on some very carefully standardized pig iron.

Results in the first column are by using the Gibbs method.

In the second column by modified Willliams method.

In the third by old Williams method, using the MnO_2 theory.

	Sample No.	Percentage of manganese.		
Iron ores	1	1.38	1.39	1.11
	2	1.84	1.84	1.51
	3	1.08	1.06	0.91
	4	1.34	1.35	1.20
	5	0.10	0.12	0.08
	6	2.87	2.87	2.14
	7	2.07	2.07	1.83
Pig iron	8	0.415	0.41	0.37
	9	0.442	0.44	0.38
	10	0.97	0.99	0.81

In working on ores carrying large amounts of silica it is advisable to dissolve the sample in hydrochloric acid and evaporate down to dryness, then moisten with hydrochloric acid and heat until the mass softens, and then add a few cubic centimeters of strong nitric acid; evaporate again until chlorine is driven out and then add hot water and filter off the silica and evaporate filtrate and determine manganese as usual.

I wish to acknowledge my thanks to Mr. W. Walley Davis, chief chemist, for his suggestions in regard to arranging the analytical data for publication.

VA. IRON, COAL, AND COKE CO., CROZER LABORATORY, ROANOKE, VA.

ON TRIVALENT CARBON.

(THIRD PAPER).[1]

BY M. GOMBERG.

Received July 5, 1901.

IT has been shown in the papers published by me on this subject that by the action of metals upon triphenylchlormethane the halogen can be removed quantitatively and that there results an extremely unsaturated hydrocarbon. From the behavior of this substance towards halogens and towards oxygen, the conclusion was drawn that it is an unsaturated radicle, triphenylmethyl. It was shown that the same body results whether carbon disulphide, benzene, ether, or acetic ether is employed as a solvent. It was stated that in the case of the first two mentioned solvents the unsaturated hydrocarbon remains in solution, while with ether or acetic ester as a solvent the hydrocarbon separates in the form of large transparent crystals. This crystalline body possessed all the properties of the unsaturated hydrocarbon, and was also identical with the substance which was obtained when triphenylchlormethane in benzene was acted upon by zinc and the resulting hydrocarbon was precipitated from its concentrated solution by means of ether or acetic ester. Facts have since been discovered which necessitate a modification of this view, and I desire to publish the results even in their present incomplete state.

THE ACTION OF ZINC IN ETHER AS A SOLVENT.

When triphenylchlormethane is dissolved in absolute ether and a strip of zinc is introduced, the solution at once turns yellow and

[1] First paper: This Journal, **22**, 757; Second paper: *Am. Chem. J.*, **23**, 320.

a dark viscous mass begins to separate. After a while crystals begin to form which adhere to the zinc and to the sides of the vessel. If the reaction be carried on in a sealed tube it will be noticed that in a few days the black mass begins to diminish in quantity, and in about three weeks it will disappear completely. The solution still remains yellow but the crystals are colorless. It is impossible to get the ether and the reagents so absolutely free from moisture but that at least a few bubbles of hydrogen will be formed during the reaction.[1] The viscous mass which is formed at the beginning of the reaction is not zinc chloride, but a double salt of it with triphenylchlormethane.[2] Zinc chloride, I find, is soluble in ether, while the double salt is not. The thick yellow mass which was described under the experiments with benzene is also a double salt of a similar or of identical composition, and not a compound of zinc chloride with benzene, as has been previously supposed. Such a double salt when treated with water would give up all its chlorine to the latter, and this accounts for the somewhat misleading results which were obtained in the estimation of chlorine in the insoluble residue from benzene.[3] On allowing the ethereal solution to stand for some weeks the double salt is completely broken up by the metallic zinc, but in benzene this does not occur. There is no separation of the double salt when acetic ether is employed as a solvent for the simple reason that the salt is very soluble in this solvent.

The same double salt is formed with the greatest readiness when a solution of zinc chloride in ether or in acetic ether is added to a solution of triphenylchlormethane in benzene or in absolute ether. All attempts to bring it to crystallization have failed, but a number of other double salts of triphenylhalogenmethanes, and especially of tritolylchlormethane, were obtained in sufficient purity to establish the remarkable tendency of these halogen bodies towards the formation of double compounds with metallic salts. Substances of the following composition were obtained, and they will be fully described in a later paper:

$2(C_6H_5)_3CCl.3HgCl_2$, $(C_6H_5)_3CBr.3HgBr_2$, $(C_6H_4CH_3)_3CCl.ZnCl_2$,
$(C_6H_4CH_3)_3CCl.HgCl_2$, $(C_6H_4CH_3)_3CCl.FeCl_3$.

All these compounds are beautifully crystalline, and are charac-

[1] *Am. Chem. J.*, **25**, 320.
[2] This Journal, **22**, 761.
[3] *Ibid.*, **22**, 761.

terized by intense coloration, from yellow to red. There is no doubt that the yellow color which is imparted to the solution when zinc or any metal acts upon triphenylchlormethane is due in a large measure, but not entirely, to the formation of these double salts. The transparent yellow crystals which are formed when a solution of triphenylchlormethane in ether or in acetic ether is treated with zinc are not triphenylmethyl itself, but a compound of that with each of the two solvents respectively.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH ETHER.

Samples of the above-mentioned yellow crystalline compound were analyzed from time to time, but the results usually fell from 2 to 3 per cent. short of 100 for the sum of carbon and hydrogen. This was at first ascribed to the absorption of oxygen by the unsaturated hydrocarbon during the washing and transference of the material. I then came back to the use of benzene as a solvent. An apparatus was constructed by means of which the benzene solution of the hydrocarbon could be concentrated in a vacuum at 30° C.; ether could then be added, and the crystals that were so formed could be filtered, washed, and thoroughly dried in an atmosphere of carbon dioxide,—all these operations being conducted in the same single piece of apparatus, without any rubber connections whatever. The crystalline product obtained in this way is almost insoluble in ether. It was washed with ether from fifteen to twenty times to insure the complete removal of the accompanying products such as triphenylmethane, triphenylcarbinol, etc. The crystals are at first perfectly colorless, but soon turn pale-yellow, the color increasing with standing. Twenty grams of triphenylchlormethane give about 7 grams of the insoluble crystalline compound. Molecular weight determinations of this substance were first made and the results were fairly satisfactory as calculated for triphenylmethyl.[1] An elementary analysis, however, gave the following results:

0.2884 gram substance gave 0.9488 gram carbon dioxide and 0.1900 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	89.72
Hydrogen	6.24	7.37

[1] The determinations were made by the method of the lowering of the freezing-point, in an atmosphere of nitrogen, as carbon dioxide was found to be soluble in benzene to a sufficient degree to impair the results.

A fresh sample was then prepared in a similar way and was dried over sulphuric acid in a vacuum desiccator (previously filled with carbon dioxide) over night. It gave the following results:

0.2375 gram substance gave 0.7832 gram carbon dioxide and 0.1560 gram water.

	Per cent.
Carbon	89.94
Hydrogen	7.35

A new sample was then prepared, dried, and analyzed in the same day, but the results were almost the same.

0.2447 gram substance gave 0.8060 gram carbon dioxide and 0.1585 gram water.

	Per cent.
Carbon	89.83
Hydrogen	7.25

The next sample was prepared by the addition of a mixture of acetic ether and acetic acid instead of absolute ether, in order to hold better in solution any zinc salts which might possibly have accompanied the previously mentioned samples. This sample was washed first with acetic ether and then with absolute ether. It looked whiter and more distinctly crystalline than any before obtained, but the analysis gave figures for carbon and hydrogen, the sum of which was only 95.67 per cent. The close concordance of the first three samples, and the fact that when acetic ether, which carries almost twice as much oxygen as ethyl ether, is used for precipitating the hydrocarbon, a product proportionately richer in oxygen is obtained, suggested the idea that the substances analyzed must be compounds of the hydrocarbon with the solvents.

	Calculated for $2(C_6H_5)_2C + (C_2H_5)_2O$.	Found. I.	II.	III.
Carbon	89.93	89.72	89.94	89.83
Hydrogen	7.21	7.37	7.35	7.25

That we have here such a compound is proved by the following experiment: 0.9430 gram of the ether compound was placed in a platinum boat and gently heated at 70° C. in a tube, in a stream of carbon dioxide. The loss in weight was 0.1090 gram.

	Calculated for $2(C_6H_5)_2C + (C_2H_5)_2O$.	Found.
Loss	13.22	11.56

The escaping ether was easily identified by its odor, and a few droplets were also condensed in a small U-tube which was sealed on to the further end of the tube. The amorphous yellow residue

shows all the properties of the unsaturated hydrocarbon. It absorbs iodine with great eagerness ; a solution of it, when exposed to air, gives the triphenylmethyl peroxide. An analysis of the residue gave the following results :

0.1620 gram substance gave 0.5520 gram carbon dioxide and 0.1020 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	92.93
Hydrogen	6.24	7.05

It remains yet to be settled whether this residue represents pure triphenylmethyl or a mixture of it with some of its decomposition products.

COMPOUND OF THE UNSATURATED HYDROCARBON WITH ACETIC ETHER.

A reaction entirely analogous to the one described above takes place when acetic ether is substituted for absolute ether. A compound of the unsaturated hydrocarbon with acetic ether is at once formed when triphenylchlormethane, dissolved in the ester, is treated with zinc. It is also produced when the metal is allowed to act upon the halogen compound dissolved in benzene, and to the concentrated solution acetic ether is added. The sample which furnished the results given below was prepared by the second method ; it was washed fifteen times with acetic ester, and was thoroughly dried in an atmosphere of carbon dioxide.

0.3160 gram substance gave 1.0180 gram carbon dioxide and 0.2080 gram water.

	Calculated for $2(C_6H_5)_3C + CH_3CO_2C_2H_5$.	Found.
Carbon	87.74	87.86
Hydrogen	6.69	7.37

The compound of the hydrocarbon with the ester is perfectly colorless when first prepared, but soon turns pale-yellow. It is more stable than the corresponding ether compound, and can be kept much longer without discoloration. It can be obtained in large crystals or in the form of a granular crystalline powder. On heating, it loses the ester.

1.1170 gram substance lost at 100° C. 0.1575 gram.

	Calculated for $2(C_6H_5)_3C + CH_3CO_2C_2H_5$.	Found.
Loss	15.50	14.10

The escaping acetic ester was condensed and identified as such.

The residue, after driving off the ester, looked like that obtained from the ether compound. It was amorphous, yellow, soluble in benzene and in carbon disulphide ; it absorbed iodine and gave the peroxide. An analysis gave the following results :

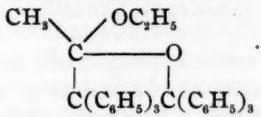
0.2135 gram substance gave 0.7250 gram carbon dioxide and 0.1322 gram water.

	Calculated for $(C_6H_5)_3C$.	Found.
Carbon	93.76	92.61
Hydrogen	6.24	6.93

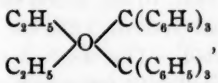
It will be noticed that in both instances the per cent. of carbon is somewhat low for triphenylmethyl. This may be accounted for by a slight oxidation, but I have no explanation at present as to the cause of the rather high per cent. of hydrogen.

WHAT IS THE NATURE OF THESE COMPOUNDS?

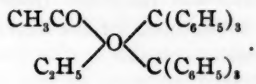
It is impossible to tell at this time whether in these two instances the ether and the acetic ester are those of crystallization or of constitution. Such a distinction is at best but an arbitrary one. One would expect that ether of crystallization would be easily driven off *in vacuo* over sulphuric acid,—which is not the case in this instance. From the extreme unsaturation of the hydrocarbon it may be assumed that it might add itself to acetic ester, giving a body something like this :



But it could hardly be expected that mere heating at 80°–100° C. would break up a chain of three carbon atoms in such a way as to regenerate the ester. Then, again, the combination with ethyl ether precludes any such addition theory in that instance. If it is not ether of crystallization, then the following constitution of that body suggests itself :



and the acetic ester compound may be supposed to have the corresponding constitution



In support of such a constitution might be cited the remarkable avidity of the hydrocarbon for oxygen, and the possibility of oxygen to act as tetravalent. Such a possibility was foreshadowed by van 't Hoff as long ago as 1877.[1] There has since been accumulating a considerable amount of evidence of physical nature pointing to such a possibility. In connection with this may be mentioned the recent work of Kanonnikow. From a study of alcohols and ethers at their critical condition, Kanonnikow[2] comes to the conclusion that in these compounds, under these conditions, the oxygen behaves as if it were tetravalent. The extreme unsaturation of triphenylmethyl presents an excellent opportunity to test the theory of the tetravalence of oxygen. The above formulas for the two compounds must be looked upon, at present, as a mere suggestion. It is my intention to extend this study to other oxygen compounds, as well as to nitrogen derivatives, and I beg to reserve this field for further work.

CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN,
June 29, 1901.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 56.]

THE ATOMIC WEIGHT OF ANTIMONY.

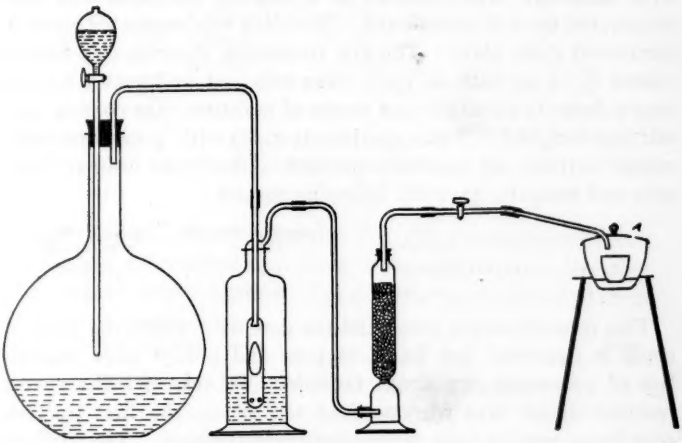
BY G. CLAUSEN FRIEND AND EDGAR F. SMITH.

Received June 8, 1901.

KNOWING that antimony oxide could be completely expelled from its combinations in a current of hydrochloric acid gas it appeared probable that a new ratio might be established for antimony, by exposing potassium antimonyl tartrate to the action of this gas. It will be recalled that by this procedure the atomic weights of molybdenum and arsenic had been previously determined in this laboratory. In these particular instances sodium molybdate and sodium pyroarsenate were exposed in porcelain boats, at a moderate heat, to the action of the gas, and from the weight of the residual sodium chloride the respective atomic weights were calculated. The method of work adopted with these metals was pursued with potassium antimonyl tartrate, but it was soon discovered that as carbon dioxide and water escaped the salt swelled up and was projected from the boat, so that a double crucible was substituted for the latter. On trial this de-

[1] "Ansichten über die organische Chemie."
[2] *J. Russ. phys. chem. Soc.*, **33**, 197.

vice proved to be perfectly satisfactory, and it was possible in a crucible No. 00, from 1 to 1¼ inches in height, to operate with as much as 3 grams of material. The appended sketch represents the apparatus in detail.



A steady stream of hydrochloric acid gas was generated in the large flask by acting with pure, concentrated, sulphuric acid upon hydrochloric acid of like character. The gas was sufficiently dried by its passage through sulphuric acid and a column of calcium chloride and then introduced through a porcelain delivery tube into the crucible. The smaller crucible was supported in in the larger one upon a perforated porcelain plate. The lid of the larger crucible had two openings, one for the entrance, and the other (A) for the exit of the excess of acid gas. Platinum crucibles should not be used; they are very severely attacked by the acid vapors.

In the experiments the dry gas was passed over the salt in the smaller crucible for half an hour, before any heat was applied. At the expiration of this period a small flame was placed under the crucible and it was heated to 150° for two hours, after which the temperature was gradually increased until the outer crucible showed a dull red color. This temperature was maintained until all of the volatile matter was expelled, when a stream of oxygen was substituted, for half an hour, for the acid. Most of the car-

bonaceous material was removed in this way, when the acid vapor was again introduced and the crucible contents allowed to cool in it. As the residual potassium chloride contained some carbon, it was dissolved in water and the solution filtered. The filtrate, with washings, was collected in a weighed platinum dish and evaporated upon a water-bath. The dish was supported upon a perforated glass plate. The dry potassium chloride was finally heated in an air-bath to 150°, then removed and gently heated over a flame to expel the last traces of moisture. On cooling, the salt was weighed. Two experiments made with potassium antimonyl tartrate, not especially purified, and with an ordinary balance and weights, gave the following results :

	Salt. Grams.	Potassium chloride. Grams.	Atomic weight of antimony.
1	2.0358	0.4691	120.44
2	2.5919	0.5973	120.41

This concordance in result and the ease with which the method could be executed, led us to prepare and purify large quantities of potassium antimonyl tartrate. To this end the purest commercial salt was recrystallized ten times, the first fraction only being used in each subsequent crystallization. The final 50 grams, intended for experiment, were dried at 150° for a period of sixteen hours. A weight was taken and the mass then again heated, cooled, and reweighed. There was no variation in the weight. This material was carefully tested for impurities (*e. g.*, arsenic, sodium, silica, etc.), and was found free from them. Portions of it were then acted upon as outlined in the preceding paragraphs.

The balance used in the subsequent experiments was constructed for atomic weight work by Troemner. It is sensitive to $\frac{1}{40}$ of a milligram with or without load. The weights of brass and platinum were carefully calibrated. All weighings were reduced to the vacuum standard. The specific gravity of potassium chloride was taken as 1.995 and that of the tartar emetic as 2.6 (Beilstein). The atomic weights used in the calculations were $O = 16$, $H = 1.008$, $C = 12$, $K = 39.11$, and $Cl = 35.45$. The results obtained with the pure material and with the observance of all the necessary precautions were :

	Potassium antimonyl tartrate. Grams.	Potassium chloride. Grams.	Atomic weight of antimony.
1	1.19481	0.27539	120.345
2	1.57004	0.36186	120.359
3	2.00912	0.46307	120.351
4	2.04253	0.47073	120.379
5	2.16646	0.49935	120.341
6	2.25558	0.51982	120.385
7	2.61255	0.60215	120.350
8	2.95272	0.68064	120.311
			Mean = 120.353

Maximum = 120.385
Minimum = 120.311

Difference 0.074

The barium and silver antimonyl tartrates crystallize well and the hope was entertained that these salts might also be included in the circle of experimentation but thus far the results with them have not been satisfactory.

UNIVERSITY OF PENNSYLVANIA.

THE CHEMICAL NATURE OF ENZYMES.

BY P. A. LEVENE.

Received May 18, 1901.

There is comparatively little known about the chemical nature of the enzymes. In fact it is only in recent years that some attention has been given to these substances. Even the supposition that enzymes are of a proteid nature is not based on irrefutable evidence. Nevertheless, this is generally accepted. Very recently Hans Friedenthal claims that the enzymes possess the nature of nucleo-proteids.

It is chiefly in view of this last research that I have published some of the results of the investigation on the chemical nature of enzymes. The object of this work is to determine whether enzymes are actually of proteid nature. It was established during the last few years by the researches of Morochowetz, Lawrom, and Kutcher that proteids can be digested by means of trypsin to such an extent that the product no longer gives the biuret test, in other words the entire proteid material is decomposed. It was also demonstrated by Gulewitch that trypsin does not act on nitrogenous substances of non-proteid nature. Hence it seemed possible to test the proteid nature of enzymes by subjecting them to tryptic digestion.

The statement has, however, been made that some enzymes are destroyed even by a comparatively short digestion with trypsin, but this statement has also been contradicted. It therefore appeared advisable to repeat these experiments.

Popow has demonstrated that trypsin decomposes nucleoproteids, splitting off their phosphorus as phosphoric acid, and it seemed therefore possible to ascertain by means of tryptic digestion, whether enzymes were of the same nature as nucleoproteids.

I performed my first experiment in September, 1899. Several pounds of fresh pancreas glands were chopped, treated with 0.5 per cent. solution of sodium carbonate and a large quantity of chloroform. The mixture was allowed to stand over night. It was then strained through gauze and the liquid divided into several flasks, more chloroform added, and then placed in the thermostat at 40° C. The contents of the flasks were well shaken every day. After a couple of weeks of digestion the contents of the flasks were filtered, the filtrate transferred into acid bottles, a considerable quantity of chloroform added and placed in a very warm room. The bottles remained there until May, 1900.

The solution which was very dark in color, was then decolorized by means of animal charcoal, and tested for biuret and gave a negative result.

Another part of the same decolorized liquid was treated with a great excess of alcohol and the whole precipitate thus obtained tested for biuret without result.

From the above negative tests it was assumed that all the proteids of the original extract were decomposed. In order to test how far the decomposition of the nucleic acid went, a determination of the phosphorus in the form of organic and inorganic compounds was made.

In 25 cc. of the solution the phosphoric acid was precipitated by means of magnesia mixture. The precipitate slightly colored was redissolved with hydrochloric acid and reprecipitated with ammonia. The magnesium pyrophosphate weighed 0.257 gram.

Another 25 cc. of the same liquid was evaporated to dryness, and the residue fused with sodium carbonate and potassium nitrate. The phosphorus was estimated in the usual way. The magnesium pyrophosphate weighed 0.249 gram.

This experiment demonstrated that trypsin is able to decom-

pose absolutely the nucleo-compounds of the pancreas, as well as the proteids. This solution of the self-digested pancreas extract, however, has no proteolytic activity.

It was then attempted to subject trypsin to self-digestion for a shorter period, so as either to break up all the nucleins and leave some proteid material intact or vice versa.

Grubler's trypsin was used for these experiments. About 3 grams of the substance were treated with 150 cc. of 0.5 per cent. solution of sodium carbonate and allowed to stand six weeks. At the end of that time the mixture was filtered. The filtrate gave a positive though very weak biuret test, and possessed tryptic activity. 50 cc. of the solution were used for the estimation of the total phosphorus, another 50 cc. for the estimation of phosphorus in the form of phosphoric acid. The total phosphorus weighed 0.00125 gram and the phosphorus as phosphate weighed 0.0012, thus showing the absence of nucleo compounds in the solution, and still the solution contained the proteolytic enzyme.

In experiment No. 2, 30 grams of trypsin (Fairchild) were treated with 50 cc. of 0.5 per cent. solution of sodium carbonate (a great excess of chloroform added as an antiseptic), and allowed to stand in an incubator.

After three weeks of self-digestion part of the mixture was filtered and tested for proteolytic activity. The result was positive. In 25 cc. of the filtrate, the total phosphorus was estimated, and it weighed 0.0162 gram. In another 25 cc. portion the phosphorus is estimated as phosphate; it weighed 0.0131 gram, thus showing the presence of traces of nucleo-compounds.

After four weeks of self-digestion another experiment was made similar to the former. The solution still possessed its proteolytic properties. 10 cc. of it contained 0.00715 gram phosphorus. Another 10 cc. of the same contained 0.00628 gram phosphorus as phosphate, again showing the presence of a slight amount of nucleo-compounds.

The experiment was again repeated after six weeks of self-digestion. The solution was still active and gave the test for biuret. 10 cc. of the solution contained 0.00715 gram total phosphorus. 10 cc. of the same contained 0.00663 gram phosphorus as mineral phosphates, thus containing scarcely any nucleo-compounds and still possessing proteolytic activity. These experi-

ments would scarcely justify the conclusions of Freslenthal that trypsin is a nucleo-compound.

The fact that only those solutions were active which gave a positive biuret test would seem to indicate that trypsin is of a proteid nature. However, in some cases the biuret test was scarcely perceptible, and yet the solution of the self-digested trypsin still contained the active ferment.

Experiments on other enzymes in the same direction are now in progress.

I wish to express my indebtedness to Doctor D. Sculley for the assistance received from him.

CONTRIBUTIONS TO THE KNOWLEDGE OF REVERSIBLE REACTIONS.

By W. N. Stull.

Received June 17, 1901.

THE object of the study outlined in the following pages was primarily to investigate the positions of the points of equilibrium when acid solutions of certain metals were treated with hydrogen sulphide, and to determine the influence of agitation and temperature upon these points. Incidentally to this main purpose, it was thought desirable to ascertain under what conditions the separation of certain metals, such as zinc and cadmium, could most accurately be effected by hydrogen sulphide. The author has been unable to find any account of accurate determinations upon this latter point, though the common method of separating zinc and cadmium by hydrogen sulphide is practiced in almost all laboratories.

At the beginning it was found that the attainment of equilibrium with acid solutions of zinc and cadmium presented serious difficulties, since the reactions are exceedingly slow, and, in fact, in no case was complete equilibrium reached even after the solution had been treated with a rapid stream of hydrogen sulphide for many hours. As the work advanced, therefore, the importance of the speeds of the reactions became more and more apparent, and as a result this factor became the chief object of study, and incidental thereto, the effects of temperature and agitation.

Since the author must discontinue the work for a time to devote himself to other duties, it is deemed best to publish the results, incomplete as they are, on account of their bearing upon practi-

cal problems of analysis. At a later date he hopes to continue the work and discuss it with reference to the theory of equilibrium and mass action. Thus far the work has extended only to zinc and cadmium in hydrochloric and sulphuric acid solutions.

Apparatus and Precipitation.—The solution of the metal was contained in two tubes immersed in a water-bath, kept at constant temperature by a thermostat. Washed hydrogen sulphide was passed into the tubes at the rate of about 4 liters per hour. At the end of any period of time selected, a portion was filtered and the zinc or cadmium remaining in solution determined. The zinc was determined volumetrically by the ferrocyanide method of Lyte. Cadmium was determined as the sulphide. When temperatures higher than 30° were used a tube partially filled with water was placed in the bath and connected between the gas-generator and the precipitation tubes so as to compensate so far as possible for the loss of water from the solution by evaporation.

SERIES I. ZINC IN HYDROCHLORIC ACID SOLUTION.

Column I indicates the number of the determination, II the time in hours, III the per cent. of free hydrochloric acid, and IV the per cent. of zinc remaining in solution. The temperature was 20°.

I.	II.	III.	IV.
1	0.5	0.06	4.31
2	1.0	0.57	3.84
3	1.5	0.98	3.48
4	2.0	1.53	3.00
5	2.5	1.76	2.78
6	3.0	1.92	2.63
7	3.5	2.14	2.42
8	4.0	2.27	2.32
9	4.5	2.35	2.25
10	5.0	2.48	2.13
11	5.5	2.65	1.98
12	6.0	2.72	1.92
13	6.5	2.86	1.81
14	7.0	2.98	1.69
15	7.5	3.18	1.55

It will be observed that at the end of seven and one-half hours, precipitation was still taking place and at a rate which indicated that equilibrium was yet far removed.

SERIES II. ZINC IN SULPHURIC ACID SOLUTION.

The conditions of precipitation were the same as in Series I. Here, as in Series I, the zinc sulphide precipitated was perfectly white, the zinc used being a very pure specimen that showed no impurity save a trace of iron, and an amount of carbon residue too small for determination. Column II shows the time in hours, column III the per cent. of free sulphuric acid, and IV the amount of zinc remaining in solution.

I.	II.	III.	IV.
1	0	1.09	2.29
2	1	2.12	1.60
3	2	2.65	1.25
4	3	3.40	0.75
5	4	3.95	0.38
6	5	4.26	0.18
7	6	4.38	0.07
8	7	4.47	0.03

At the end of seven hours precipitation was still going on, although very nearly complete. The solution contained about 4.50 per cent. of free acid. In order the better to compare the restraining action of the two acids, it was thought desirable to use solutions which would contain approximately the same amounts of zinc at the beginning and at the end of the precipitation. The results are shown in Series III.

SERIES III. ZINC IN SULPHURIC ACID SOLUTION.

I.	II.	III.	IV.
1	1	0.95	4.24
2	2	1.76	3.68
3	3	2.28	3.35
4	4	2.88	2.94
5	5.5	3.49	2.54
6	6.5	3.77	2.35
7	7.5	4.18	2.08
8	9.0	4.61	1.80
9	10.5	5.25	1.37

The course of the reaction in the presence of free sulphuric acid is very similar to that in the presence of free hydrochloric acid. The curves representing time and precipitation in the two cases are very nearly parallel. Comparing the amounts of free acids at the end of equal times (seven and one-half hours) in Series I and III, it may be observed that sulphuric acid exerts little less re-

straining influence than hydrochloric, since the amount of the former exceeds the latter by only about 1 per cent.

Influence of Time.—It seemed desirable to determine the influence of time, if any, upon the amount of precipitation, and to this end four experiments were performed with the same solution. In the following table, column II gives the time during which the gas was passed into the solution, column III the time in hours that the solution was allowed to stand before filtering, IV the free hydrochloric acid, and V the zinc remaining in solution. In 3 the solution was shaken one and one-half hours before filtering. Of course the tubes were kept tightly stoppered while standing. At the ends of the respective times the solution still contained much free hydrogen sulphide.

SERIES IV.

I.	II.	III.	IV.	V.
1	1	0	2.82	1.83
2	2	12	3.11	1.57
3	1	13.5	3.10	1.57
4	3.5	13.5	3.87	0.89

The results show some precipitation after the hydrogen sulphide has been stopped, but probably a three-sided equilibrium of hydrogen sulphide, hydrochloric acid, and zinc chloride is reached within a few hours, and this does not seem to be affected by agitation.

Influence of Agitation.—In order to determine more fully the effect of agitation upon the rate of precipitation, portions of a solution containing 4.86 per cent. of free and combined hydrochloric acid were treated in two tubes, with hydrogen sulphide. In one of these tubes was a stirrer kept in rapid motion by a hot-air engine. The tubes were kept at the same temperature, 20°. Column V shows the amounts of zinc remaining in solution in the tube not provided with a stirrer, at the ends of the respective periods, and column IV gives the zinc in the solution stirred. In order to reduce the effect of agitation due to the gas itself, the rate of flow was made considerably less than that used in the other series.

SERIES V.

I.	II.	III.	IV.	V.
1	1	4.86	3.53	3.65
2	2	...	2.85	2.80
3	3	...	2.15	2.23
4	4	...	1.73	2.01

The results confirm that of experiment 3, in Series IV, and show that agitation has very little influence upon the rate of precipitation.

Influence of Temperature.—To determine the influence of temperature upon the rate of precipitation, portions of the same solution of zinc chloride were treated at 20° and 50°, respectively, for five hours with hydrogen sulphide flowing at the same rate in each case. Column II, in Series VI, gives the temperature, column III the time, and column IV the zinc remaining in solution. The results show that change in temperature within moderate limits has very little influence upon either the rate of precipitation or the point of final equilibrium.

SERIES VI.

I.	II.	III.	IV.
1	20°	5	1.41
2	50°	5	1.49

Cadmium.—A solution of cadmium chloride was made by dissolving the pure metal in hydrochloric acid. It contained 9.47 per cent. of cadmium and the total acid was 11.33 per cent. The solution gave a pure yellow precipitate with hydrogen sulphide which was free from zinc. The only impurity found was a trace of iron. This solution was treated with hydrogen sulphide in the same way as those of zinc. At the ends of the periods chosen portions were filtered and the cadmium remaining in solution was determined as sulphide, with the usual precautions. In the following table column II contains the time in hours, column III the per cents. of free acid, and IV the per cents. of cadmium remaining in solution.

SERIES VII.

I.	II.	III.	IV.
1	2	8.72	4.00
2	3	9.40	2.96
3	4	9.84	2.42
4	5	10.15	1.81
5	7	10.19	1.75
6	8	10.26	1.64

The general trend of the curve of precipitation is the same as that for the precipitation of zinc from a solution of the chloride, as may be seen by a comparison of the above results with those of Series I, though the approximate equilibrium in the case of cad-

mium is reached much sooner. A comparison of the two is of interest from the analytical point of view. Zinc is by no means all precipitated after many hours from a solution containing 3.18 per cent. of free hydrochloric acid, and the precipitation of cadmium is not complete in a solution containing 10.26 per cent. of this acid. The range of the strength of acid within which it might be considered possible to separate the two metals by precipitation with hydrogen sulphide is, therefore, considerably less than 7 per cent., and a consideration of the curves would lead one to doubt whether it is possible to separate them by a single precipitation with any strength of hydrochloric acid.

Cadmium in Sulphuric Acid Solution.—Cadmium sulphate was made by heating pure cadmium nitrate with pure concentrated sulphuric acid until all trace of nitric acid had disappeared. Experiments showed that cadmium could be completely and quickly precipitated at 20° C. from any strength of sulphuric acid solution. Attention was directed, therefore, to its precipitation at higher temperatures, and for this purpose 85° was the point chosen as convenient. A solution containing about 15 per cent. of free acid and 9 per cent. of cadmium sulphate was treated with hydrogen sulphide at the usual rate for three and a half hours. The cadmium remaining in 13 grams of the solution at the end of this time was only 0.0004 gram, while the amount of free acid as shown by titration was 18.66 per cent.

A second solution containing 9 per cent. of cadmium sulphate and 20 per cent. of free acid was treated with hydrogen sulphide for three hours and at 85°. The cadmium remaining in solution was found to be about the same as above, or only a trace, showing that this metal can be practically completely precipitated from a hot solution containing 22.8 per cent. of free sulphuric acid, this being the amount found by direct titration.

By a comparison of these results with those obtained in Series III, zinc sulphate, it will be seen that while the precipitation of zinc had practically ceased when the free sulphuric acid had reached 5.25 per cent., cadmium is totally precipitated at 85° in the presence of 23 per cent. of free acid. In other words the range of possible complete separation of zinc and cadmium when sulphuric acid is used is at least 17 per cent., or three times what it is when hydrochloric acid is used, and with precipitation at common room temperature the range would probably be much greater.

In view of the fact that cadmium sulphide is soluble in dilute boiling sulphuric acid, the common method of separating cadmium and copper being based upon this fact, it was deemed rather surprising that complete precipitation had taken place at such a high temperature and in the presence of such a quantity of free acid. The following experiment makes clear this seeming anomaly: A portion of the solution, in the last experiment with cadmium sulphate, which contained only a trace of cadmium immediately after the stream of hydrogen sulphide was stopped, was left in contact with the precipitated cadmium sulphide at 85° for half an hour. At the end of that time the solution, now almost free from the odor of hydrogen sulphide, had dissolved 1.8 per cent. of its weight of cadmium sulphide. This result in connection with what has preceded seems to show that the complete precipitation of cadmium as sulphide depends chiefly upon the saturation of the solution with hydrogen sulphide, the temperature and strength of the acid being of only secondary importance. Direct experiment showed that when pure washed cadmium sulphide is allowed to remain in contact with cold dilute sulphuric acid (20 per cent. H_2SO_4) for several hours, it is to a very marked degree dissolved.

I wish to take this opportunity to express my sincere thanks to Dr. W. S. Hendrixson, at whose suggestion this work was undertaken and to whose kind advice and aid any success which this little study may have attained is largely due.

IOWA COLLEGE, GRINNELL,
June 10, 1901.

NEW BOOKS.

ATOMS AND ENERGIES. By D. A. MURRAY. New York: A. S. Barnes & Co. 1901. 202 pp. Illus. 12mo.

The author of this book was some time instructor in the Government Shogyo Gakko, Kyoto, Japan, and he is at present pastor of a Church in a Western city. He claims that the "changed conceptions of the nature of fundamental atomic phenomena" presented in this book, must create a "complete revolution in our thinking along many lines of physical research," and for those who accept his visionary lucubrations this claim will certainly be justified.

According to the author, atoms are all identical in substance

and differ only in size and shape; he defines an atom as "an Impenetrable Expanse of the ability to Modify and be Moved by Energy." He dwells at length upon the shapes of atoms, for "the one element of Shape in the atom is capable of determining all the varieties of result found in combinations." Thus iron and gold are identical in essence, but their diverse qualities are determined by diversity in shape and size of their atoms. The book contains several illustrations showing the shape of atoms, and they resemble the building blocks used by children and the diagrams of dressmakers. Notwithstanding much space is given to the shape of atoms (pages 43 to 58), the fact that they are endowed with weights is generally ignored!

These atoms are influenced by two energies only, one attracting and one repelling, but "Energy" is not a mode of motion, it is a "distinct Entity." "Adhesion, Cohesion and Chemical Affinity in all its myriad forms," are simply different "operations of Gravitation," and the "key to the solution is to be found in the infinite factor which comes into operation when the atoms are in actual contact with each other." The different kinds of contact are thus explained: "When not in contact we have the Gaseous state; when but a single point of contact, the Liquid state; when so many points of contact that there is rigidity, the Solid state; when face to face contact, Chemical Combinations."

The author demonstrates to his satisfaction that the interstellar Ether is identical with Energy; he concludes that "the Ether is simply Energy as an Entity."

It is difficult in reviewing a book of this character to avoid doing the author injustice, but we have endeavored to prevent this by citing almost exclusively his own words. The work is endorsed (in an Introduction) by a gentleman who has been successful as an archæologist and anthropologist, especially in exploring Mexico, but his pursuits have not especially qualified him for judging a treatise on physical science. He says, however, that the work "will stimulate thought."

HENRY CARRINGTON BOLTON.

QUANTITATIVE CHEMICAL ANALYSIS, ADAPTED FOR USE IN THE LABORATORIES OF COLLEGES AND SCHOOLS. By FRANK CLOWES, D.Sc. (LOND.) AND J. BERNARD COLEMAN, A.R.C.Sc. (DUBLIN). Fifth edition. Philadelphia: P. Blakiston's Son & Co. 1900. xxiv + 592 pp. Price, $3.50.

This is a standard laboratory guide in many of the English

colleges and has also received favor on this side the water. The subject-matter is arranged under sixteen sections. The first three of these describe chemical apparatus, careful chemical manipulation, the determination of specific gravity, boiling-point and melting-point, and the preparation of pure substances. Section IV is arranged so as to be progressive in point of difficulty and includes directions for the gravimetric determination of the more important bases and acids. Volumetric analysis is taken up in Sections V–VIII, beginning with the calibration of burettes, flasks, etc. This could be considerably improved by calling attention more prominently to the necessity of reducing the weight of water to "in vacuo," and giving the correction to be applied for the contraction and expansion of glass. The preparation of, and use of normal solutions are fully explained by practical examples. Section IX is devoted to metallurgical analysis and is the most faulty part of the book. This is probably due to the inferiority of the English to the American methods of metallurgical analysis. For example in this book, zinc is determined in its ore volumetrically by the use of sodium sulphide solution, and silicon in pig iron by evaporation to dryness with nitric acid, etc. The fire assay for lead, silver, and gold, is condensed "past all understanding" into five pages. Sections X and XI are very much better and cover water, food, and soap analysis and the valuation of tanning materials. The methods given for the latter purpose are excellent. Organic analysis and the determination of molecular weights are taken up in Section XII, and the concluding sections treat of simple gas analysis. A collection of tables and miscellaneous matter is appended. The book is well printed and freely illustrated. The methods all through are fully explained and the calculations involved in the analyses are made clear by examples. The entire absence of any references to the periodical literature of the profession and the failure to give credit for the methods, except in rare instances, do not add to the value of the book. Even students should be taught to avail themselves of this wealth of information and experienced chemists usually wish to know sufficient of the history of their methods to enable them to consult the original description and subsequent modifications.

RICHARD K. MEADE.

THE MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS. By FRANCIS H. JENNISON, F.I.C., F.C.S. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1900. iii + 136 pp. 16 plates. Price, $3.00.

Mr. Jennison has written an interesting and useful book on an important industry whose literature heretofore has consisted of a few scattered chapters or an occasional paper. In the introduction, the author points out the necessity of an intelligent comprehension of the chemistry, constitution and properties of the colors and the subject is treated consistently from this standpoint. This systematic discussion of the industry furnishes a safer guide for the color-maker than empiricism. The few formulas given are types. In the author's words, "It is by far the best plan for each color-maker to carefully examine the color and devise the most rational way to produce the best results, ... for what works well in one man's hands in a certain place does not, ... work well with another man in another place."

Three chapters, I, II, and VII, are given to a consideration of the artificial color molecule, beginning with the general principles of synthetic chemistry; then a description of the most important classes of the colors with examples; finally, the auxochromes, salt-forming groups, absorption and the function of tannic acid and tartar emetic are considered.

"The Nature and Manipulation of Artificial Colors" is the caption of a chapter on the forms of colors as they appear in the trade with certain recommendations of particular wares of various makers.

A chapter each is given to the description of lake-forming bodies for acid and for basic colors, lake bases, red lakes, other lakes, the insoluble azo colors as pigments, the general properties of lakes, washing, filtering and finishing, matching and testing.

It is an attractive volume embellished with sixteen plates bearing slips of paper coated with lake pigments. These should have been securely gummed, for being secured at only one end they are easily disarranged. Misprints are rather numerous and some astonishing errors are noted: as, "normal hexane, $CH_3CH_2CH_2$-CH_2CH_3, isohexane, $CH_3CH_2CH_2\langle^{CH_3}_{CH_3}$", page 5; "cinnamic acid, $C_6H_2Cl_2\langle^{COOH}_{COOH}$, phenylacrylic acid, $C_6Cl_4\langle^{COOH}_{COOH}$", page

12, and others. "Palmatic" acid, pages 76 and 54, seems to have displaced palmitic. C. W. PARMELEE.

GLUE AND GLUE TESTING. BY SAMUEL RIDEAL, D.Sc. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1900. viii + 144 pp. Price, $4.00

The author aims to give the more important facts connected with the manufacture of glue. In Chapter I the constitution and properties of glue and allied substances are dealt with. This is a topic which most books on this subject do not go into to any great extent. The relations between glue and gelatine are discussed pretty thoroughly, and a table of gelatine-producing substances is copied from Allen. The next chapter considers the manufacture of glue from the raw materials. Starting with the stock it is carried through the liming, washing, cooking, and clarifying process. The need of careful liming and a good supply of water for washing purposes are both emphasized. The use of antiseptics for prevention of putrefaction is mentioned briefly. A few different kinds of kettles, boilers, and evaporators are described and illustrated. Chapter III, in a few pages, states the various ways in which glue is used and the qualities necessary for the different grades. The next thirty pages have to do with gelatine, giving its properties, tests, etc., and describing different forms and the various uses to which they are put.

The chapter on glue testing is somewhat of a disappointment. The title of the book leads one to expect considerably more than is contained in the twenty odd pages given to it. The final pages on "commercial aspects" review the glue trade in general and deprecate the "antiquated policy of exclusiveness," claiming that the custom of keeping "trade secrets" entirely in the dark retards improvement, and works to the disadvantage of the business.

The book on the whole, while covering the ground pretty thoroughly, contains very few original ideas. Liberal quotations are made from similar works. W. B. BROWN.

SELECT METHODS IN FOOD ANALYSIS. BY HENRY LEFFMANN, A.M., M.D., AND WILLIAM BEAM, A.M., M.D. Philadelphia: P. Blakiston's Son & Co. 1901. 383 pp. Price, $2.50.

This is one of the most concise and up-to-date books on the subject of food analysis out. While it is intended to be adapted to the needs of advanced students of chemistry as well as the

practising analyst, yet there is nothing of the ordinary text-book style about it. To a large extent the book is a summary of methods and data scattered through the bulletins of the United States Agricultural Department, and of the A. O. A. C., the most of which are now out of print. The authors have also drawn largely upon the works of Allen and Mitchell, and the *Analyst* for considerable of the material. It is divided into two main sections, analytic methods and applied analysis.

The first section on analytic methods describes both physical and chemical operations, such as determination of melting-point, specific gravity, and methods for extraction, distillation, etc., and illustrates some of the newer pieces of apparatus for the same. In describing methods of determining melting-points no mention is made of the acoustical method which is considered very dependable by many chemists. Under nitrogen determinations the Gunning method is mentioned as the most satisfactory, and nothing is said of the straight Kjeldahl method which, for some purposes, is preferable.

Several pages are devoted to the study and identification of starches and flours, giving tables summarizing the characteristics and microscopical appearances of the different starches. In this connection are several plates in the appendix of starch granules reproduced from a government bulletin, the reproduction of which by the way is poor. The examination of food fats and oils, is discussed at some length but is incomplete in some ways.

The matter in the sections on milk, butter, and cheese, is similar to the contents of the author's excellent little book on "Milk and Milk Products," but it has been revised and made more practical, and now contains all the information necessary for the analysis of milk products.

The last 100 pages take up such subjects as the examination of tea, coffee, spices, extracts, alcoholic beverages and flesh foods.

There is an appendix containing a few tables, followed by plates of starch granules and leaves all reproduced from Bulletin 13, U. S. Department of Agriculture. The book is bound the same as the latest edition of Allen's "Commercial Organic Analysis."

W. B. BROWN.

PURE AIR, OZONE AND WATER. A practical treatise of their utilization and value in oil, grease, soap, paint, glue, and other industries. By W. B. COWELL. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1900. vii + 85 pp. Price, $2.00.

This is a small volume of 85 pages, and has to do with the applications of pure air, ozone, and water in industrial works. The author describes briefly the various uses to which air, ozone, and water may be put in technical works to aid in manufacturing processes, purifications, etc.

It is a practical book from the ordinary manufacturer's standpoint and is almost free from technicalities, but for the scientific man who is at all familiar with the methods used and principles involved in technical industries there is little new. One chapter takes up the purification of water and its uses for boiler purposes, all of which may be found in a dozen or more books.

There is an appendix which contains considerable valuable information, giving tables of temperatures, solubilities, properties of steam, and rules for measurements.

The book is well printed in large type on good paper.

W. B. BROWN.

EXPERIMENTS ARRANGED FOR STUDENTS IN GENERAL CHEMISTRY. By EDGAR F. SMITH AND HARRY F. KELLER. Fourth edition, enlarged. 88 pp., interleaved. Philadelphia: P. Blakiston's Son & Co. 1900. Price, 60 cents.

The earlier editions of this book are already familiar to many teachers, and have been characterized by the good judgment shown in the selection of experiments and the clearness of the directions given to the student. The suggestive questions on the experiments and the problems in chemical arithmetic are also to be commended.

This edition brings the book more into line with the newer ideas in teaching chemistry, by the addition of quite a number of new experiments, but this is not done at the expense of those experiments which illustrate descriptive chemistry. Judging by recent books, there seems to be a tendency to-day to neglect all of chemistry which cannot be treated quantitatively. The authors have preserved a good balance in this respect, giving a fair number of quantitative experiments, such as the determinations of the weight of a liter of chlorine, oxygen, steam, nitrogen, and ammonia; the volumetric composition of water, and of hydrochloric

acid gas; the equivalent weight of zinc, and of tin; the volumetric analysis of caustic soda, and of iron; and the specific heat of tin.

In this improved edition, the book is one of the best of the many laboratory manuals in print. JAS. LEWIS HOWE.

IRON CORROSION; ANTI-FOULING AND ANTI-CORROSIVE PAINTS. By LOUIS EDGAR ANDÉS. London: Scott, Greenwood & Co. New York: D. Van Nostrand Co. 1900. viii + 275 pp. Price, $4.00.

The extensive and important use of steel as structural material, which practically began about ten years ago, owing to the improvements in metallurgy which lowered the price of steel until its use became economical, has made the subject of this book one of great importance. Cast iron is not very easily corroded; and moreover is used in thick pieces which will stand considerable corrosion; but the opposite is the case with steel. The last preceding book on the subject was issued in 1895, and was of little value; hence much interest attaches to a new book. Like other books about other things by this author, this treatise contains practically no original matter, but gives the results of some of the more important German papers on the subject. The comparison of different passages will therefore give contradictory views on the same topic; but in such a work this is inevitable, and is nothing against it. The numerous illustrations are of very little value; and the whole treatise, which is a short one (about 80,000 words), reads as though the author were rather short of material to fill the book. The chemical part of the work is of more interest to the general reader than to the analyst, as is proper; but references to chemical literature might have been added with advantage. A rather interesting chapter is given on the composition of patent and proprietary paints, and a few pages of much value on specifications. The book is probably the best one on the subject, to date, but it is fragmentary, does not give recent English or American work on the subject, and leaves one with the impression that there is still room for a more elaborate treatise on the protection of structural metal. A. H. SABIN.

TRAITÉ DE LA FABRICATION DES LIQUEURS ET DE LA DISTILLATION DES ALCOOLS. PAR P. DUPLAIS AINÉ. Sèptieme édition, entièrement refondue par Marcel Arpin et Ernest Portier, en deux tomes. Paris: Gauthier-Villars, Quai des Grands—Augustins, 55. 1900. 1219 pp. Price, 18 francs.

This well-known work of Duplais, of which the earlier edition

was translated and appeared in an American issue, has recently been brought out in a seventh edition, which the present editors say has been thoroughly revised and in part rewritten. This applies, as the preface tells us, particularly to the first volume, that treating of the alcohols, their preparation and technology, while the second volume upon the liqueurs and alcohol containing products has not been so notably changed.

Duplais' work, as indicated by the full title given above, is mainly concerned with the manufacture of alcoholic products and this part of the work (Vol. II) will no doubt be considered as still entitled to the character long possessed by it, of being a standard authority upon the making of liqueurs and similar products.

The whole art of compounding these alcohol-containing products is explained and illustrated, the preparation of aromatic distilled waters, of tinctures and infusions, and of the nature of the volatile oils which are used and the means of recognizing their purity are covered, as is also the preparation of the sugars, syrups, and colors used. The manufacture of conserved fruits and factitious wines is also fully described and a chapter is devoted to the manufacture of carbonated waters and effervescing alcoholic liquids of artificial origin.

An alphabetically arranged account of the principal plants and drugs employed by the liqueur manufacturer is given, which puts together in convenient form quite an amount of information useful to the manufacturer.

Vol. I, devoted to the alcohols and covering the questions of fermentation and treatment of the products therefrom, is not of the same relative value. In this field there are a number of other works, both special and of general character that are more satisfactory. Thus, while this new edition of Duplais' notes Hansen's work on pure yeast cultures, it does not discuss the broader question of the part which soluble ferments play in the distilling industries. Works like "Les enzymes et leur applications" by J. Effront, published in 1898, "Soluble Ferments and Fermentation," by J. Reynolds Green, published in 1899, and the German edition of Effront's work by M. Bücheler, published in 1900, are much more valuable for this purpose. Fuller discussion of the methods of alcohol rectification and purification are also found in Barbet's "Manuel des Fabricants d' Alcools," Paris, 1894.

In its present form, Duplais' work will, however, be of value to

those interested in the liqueur manufacture and continue its reputation as a standard authority. SAMUEL P. SADTLER.

A MANUAL OF LABORATORY PHYSICS. BY H. M. TORY AND F. H. PITCHER. New York: John Wiley & Sons. 1901. 8vo. ix + 288 pp. Price, $2.00.

This little manual embodies in book form the directions for the performance of the various experiments given in the course in elementary physics at McGill University, Montreal.

The arrangement and presentation of the subject-matter is original and somewhat novel, and is, as stated in the preface, "the outgrowth of experience in teaching large classes with a limited number of instructors."

Explanations and directions for 84 experiments are given. These are distributed as follows: Sound, 10; Light, 21; Heat, 9; Magnetism, 9; Electricity, 35.

The directions for each experiment are divided into a number of sections: 1. "References" for collateral reading; 2. "Apparatus Required;" 3. "Theory of Experiment;" 4. "Practical Directions;" 5. "Example" illustrating the data and results to be obtained; and lastly there is given a blank which is to be filled out by the student after the completion of the experimental work.

The directions are brief and terse, yet quite to the point. It is evident that there has been a studied effort on the part of the authors to give just what is absolutely essential, and to do this in as few words as possible.

As in all manuals of a similar nature there is the unavoidable local flavor as to apparatus and methods. It must be said, however, that the authors have apparently succeeded admirably in reducing this to a minimum and have so presented their subject that the book can be used as a manual in any properly equipped institution.

Viewed from the standpoint of the physicist, the experiments are doubtless well selected and described; but from the chemist's point of view, it is to be regretted that the authors have omitted experiments which, it would seem, should be given to every student intending to follow up the natural sciences, as, for example, experiments dealing with polarized light, etc.

The manual is up to the usual excellence of the publishers, the paper being heavy, of good quality, and the impression neat and clear. E. M. C.

PUBLIC WATER SUPPLIES, REQUIREMENTS, RESOURCES, AND THE CONSTRUCTION OF WORKS: BY F. E. TURNEAURE, C.E., AND H. L. RUSSELL, PH.D., Professors in the University of Wisconsin. New York: John Wiley and Sons. 1901. xiv + 746 pp. Price, $5.00

The preface states that the volume is prepared with particular reference to the needs of teachers and students of technical schools; and that the specialist need look for little that is new, although it is hoped that the form in which a large amount of widely scattered information has been presented will prove a convenience to him.

An examination of the book shows it to be by far the most complete treatment of the subject which has yet appeared, resembling in many respects the elaborate German handbooks rather than the earlier American text-books on the subject. Following German precedent is particularly commendable in the very complete and up-to-date bibliography at the end of each chapter.

The study of public water supplies involves not only civil engineering and biology, but chemistry, mechanical engineering, and in fact nearly all the arts and sciences. The treatment of the subject by the authors has been facilitated because they represent respectively the two most important divisions of the subject, namely, civil engineering and biology; and as a result both the engineering and the hygienic sides of the subject have received ample consideration at every point, while the chapter on pumping machinery, which gives a comprehensive idea of the elementary principles involved, was prepared by a specialist, Mr. D. W. Mead, of Chicago.

Without attempting to take up the endless details which constitute so large a part of water supply engineering, but which, for the most part, can only be learned by actual practice, the authors have stated briefly the principles of the art, and have usually given at least an idea of the basis upon which each rests. The completeness with which even the most recent investigations and publications have been noted and used in the preparation of the work is an evidence both of the industry and thoroughness of the authors, and of the rapidity with which the publishers have put the volume through the press.

A work of this character is necessarily based largely upon previously published records, and in using such records the authors

have uniformly given credit to the original authors, which is at once simple justice to them, and a convenience to the student who wishes to know the sources of the various data given. In a few cases translations or abstracts have been referred to as if they were original articles; but this slight failing only emphasizes the general excellence of the work. The book is well printed and freely illustrated throughout.

ALLEN HAZEN.

THE MINERAL INDUSTRY: ITS STATISTICS, TECHNOLOGY AND TRADE IN THE UNITED STATES AND OTHER COUNTRIES, TO THE END OF 1900. FOUNDED AND EDITED BY RICHARD P. ROTHWELL AND COMPLETED BY JOSEPH STRUTHERS, PH.D. Vol. IX. New York and London: The Scientific Publishing Company. xxx+918 pp. Price, $5.00.

This is the ninth annual volume of a series begun in 1892 and edited by Mr. Rothwell, who died on April 17, 1901. The series has contained information of great interest and value to the metallurgist. The present volume seems to maintain the high standard of excellence reached by those preceding it. Among the special articles contained in this volume, aside from the progress reports, are those on "The Emery Deposits of West Chester County, N. Y.," by E. C. Eckel; "Production of Bromine in Michigan," by A. C. Lane; "Calcium Carbide and Acetylene," by L. K. Böhm; "Clay and its Manufacture into Brick and Tile," by H. Ries; "The Manufacture of Water-gas, with Special Reference to European Conditions," by G. Lunge; "The Utilization of Blast-furnace Gases for the Direct Production of Motive Power," by G. Lgune; The Utilization of Lignite in Germany," by P. Krusch; "The Raritan Copper Works," by L. Addicks; "Diamondiferous Deposits in the United States," by W. H. Hobbs; "A Report on Iron and Steel Metallurgy at the Paris Exhibition," by H. M. Howe; "Alloys of Iron," by H. Souther; "The Manufacture of White Lead," by P. C. McIlhaney; "A Review of the Tin Industry of the Malay Peninsula," by F. Owen.

During the year the industry increased in value $147,393,946. reaching the sum of $1,365,608,583. The total production of iron ore in the United States was 25,917,393 long tons, of pig iron 13,789,242 long tons, and of steel 10,218,572 long tons. This represents about one-third of the world's production. The coal product in 1900 was 52,131,212 metric tons antracite and 191,256,216 metric tons bituminous, a total of 243,414,163 (including cannel coal), and an increase of 14,696,584 tons over the total for 1899. The total excess of exports over imports was nearly 6,000,000 tons, an increase of about 1,750,000 tons over 1899. Our coal forms now about one-third of the world's production.

Our copper product in 1900 was 600,832,505 lbs., an increase

of 20,000,000 pounds. This is more than half the world's product. Of lead we produced 411,568 short tons, and of zinc 123,231 short tons.

Nearly all our potassium chlorate, about 6,000,000 pounds per annum, is now manufactured at home by electrolytic processes. We are the largest producers of salt (in 1900 20,738,729 barrels of 280 pounds), of gold (3,781,310 ounces), of silver (59,561,797 ounces), of phosphate rock (1,663,476 net tons), and second only to Russia in petroleum output.

This year has witnessed a great increase in the cement industry (7,991,639 barrels of Portland cement). Of the Portland cement three-quarters is produced in the states of Pennsylvania and New Jersey. The opinion is expressed that the cheapest producing territory is likely to be found in the Lehigh Valley where the industry has already had enormous development.

It is quite impossible in the space available to give an adequate idea of the vast amount of data of all sorts contained in this magnificent report of progress. E. H.

AN ELEMENTARY TREATISE ON QUALITATIVE CHEMICAL ANALYSIS. By J. F. SELLERS, A.M., Professor of Chemistry, Mercer University, Georgia. Boston: Ginn & Co. 1900. ix + 160 pp.

Within the compass of 137 pages, the author seeks to present "a course both practical and progressive * * * selected from the most recent and approved methods * * * free from the mechanical schemes in qualitative analysis * * * and conformable to the modern dissociation theory of solutions and giving * * * more than ordinary emphasis to the spectroscope."

The reviewer has read the various chapters with great interest. The impression made is that almost too much has been attempted, and that comparatively few of the students, who may pursue the course from beginning to end, as it is presented, would really become "practical analysts" or be thoroughly prepared "for advanced university work." From the reviewer's experience to attain to either of these states, would require a decidedly more exhaustive and thorough drill than seems to be intended by the author. It is hardly likely, for example, that a beginner, in carrying out the instructions for the decomposition of an insoluble silicate by the J. Lawrence Smith method, as described on page 133, would meet with much success, because of a lack of detailed directions as to how he should proceed. Other and similar instances of incomplete descriptions of analytical methods exist but they need not be pointed out, as the teacher and student will of course discover them for themselves. It only remains to say that the book is well written and will doubtless be acceptable to those who do not lay great stress upon drill in analysis.

EDGAR F. SMITH.